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CIII. *On the Purification of Radon.* *By* L. WERTENSTEIN, *Professor of Radiology at the Free Polish University, Warsaw* *.

IT is often necessary in medical applications of radioactivity, and also in purely radioactive work, to prepare very small strong sources of radon. In order to compress 100 millicuries into a volume of 1 mm.^{3}, which is a typical case, the preparation should contain 6·5 per cent. radon, and even this is not as easy as it would seem at first sight. For any work devoted to investigation of physical and chemical properties of radon, a much higher degree of purity is necessary.

During the course of some work on the determination of the volume of 1 curie of radon I have studied some methods of its purification.

My experiments were restricted to the case when radon is extracted from a solution of radium kept in an air-tight vessel and when at some stages of purification the contact of radon with organic substances is not excluded. The method of extracting radon from a finely-divided powder containing radium, described by Herschfinkiel † and Hahn ‡, seems very promising, and it is possible that it would, if properly used, yield radon of a high initial purity.

On the other hand, the purification of radon extracted from solutions could be made much easier if no organic

* Communicated by Sir E. Rutherford.

† H. Herschfinkiel, *C. R.* cxlix. p. 275 (1909).

‡ Hahn u. Heidenhain, *Ber. d. D. Chem. Ges.* lix. p. 287 (1926).

substances were used in transfer pumps, etc., by means of which the operations with radon were performed. Owing to the fact, however, that in most laboratories radon is extracted under similar conditions to those mentioned in this paper and that a radical change in the method of storing radium is a very delicate operation, I think that the following remarks may be of some general interest.

The usual impurities of radon extracted from solutions by means of transfer pumps are: hydrogen, oxygen, carbonic dioxide, mercury, and water-vapour. The presence of hydrocarbons has not been definitely proved, but their formation under the influence of α- and β-rays on organic substances is not unlikely. The removal of all these impurities is in principle very simple. In presence of heated copper and copper oxide, oxygen would combine with the copper, and hydrogen and hydrocarbons would burn to water-vapour and carbonic dioxide. With phosphorus pentoxide and potassium hydroxide used for absorbing these gases, the only impurity remaining would be the mercury vapour. This is immaterial in most cases and can be removed if necessary by the use of a convenient low temperature. In practice, however, things are not quite so simple. For ordinary chemical work the removal of gases by the use of convenient reagents may be considered as perfect. But it must be remembered that in a volume of ab. 50 c.c. the pressure due to 100 millicuries of radon is only 1·3 bar, so that, in order to obtain a good purification, the pressure of impurities should be brought down to a small fraction of 1 bar. In reality it is very difficult to reduce this pressure within a reasonable time to less than 20–30 bars, and in most cases the pressure, after the extracted radon has remained for one or two hours in presence of reagents, would be of the order of 100 bars. In some cases sparking instead of copper oxide is used, and then the residual pressure would be certainly much higher.

The incomplete purification of radon by chemical process is in itself no difficulty, provided the remaining gases do not condense at liquid-air temperature. A part of the purification apparatus may be cooled by liquid air and the uncondensed gases removed by putting the apparatus for a short time in connexion with a quickly working pump and repeating this operation four or five times.

The cooled part may be a slightly sloped tube of about 5 mm. inner diameter extending into a capillary tube. It should be made possible to separate this tube by mercury from the remaining apparatus. In this case the purified

radon, when released after removal of liquid air, can be compressed into the capillary tube. This tube sealed off through the mercury thread could constitute an appropriate source of radon. In some laboratories the cooled tube itself is sealed off while surrounded with liquid air, and radon is subsequently distilled into the capillary extension, which is sealed off in its turn. From the practical point of view both methods are equivalent, but if it is essential to know the degree of purity of radon, the first only can be used. Slight modifications of the above-described chemical methods have been used by different workers. Ramsay * found that heated lime was more effective than potassium hydroxide for removing CO_2. Debierne † has used heated lithium, which seems to remove even the last traces of gases. Rutherford ‡ obtained very good results by sparking the gaseous mixture and submitting it to the action of KOH and P_2O_5. Lind used lead chromate instead of copper oxide for the oxidation of hydrogen and hydrocarbons. All these physicists have succeeded in preparing very pure radon, as was proved by determinations of its volume and spectrum.

My experiments were in principle similar to those of Rutherford, with the difference that I have used copper oxide instead of sparking and that communications in my purification apparatus were obtained by means of mercury forks in order to avoid the evolution of CO_2 from the tap grease, while in Rutherford's work this difficulty was overcome by greasing the taps with phosphorus pentoxide. In my first experiments roughly purified radon was introduced, by means of an ordinary gas transfer pump (provided with greased taps), into the apparatus, which could be evacuated by a Töpler pump and charcoal tube.

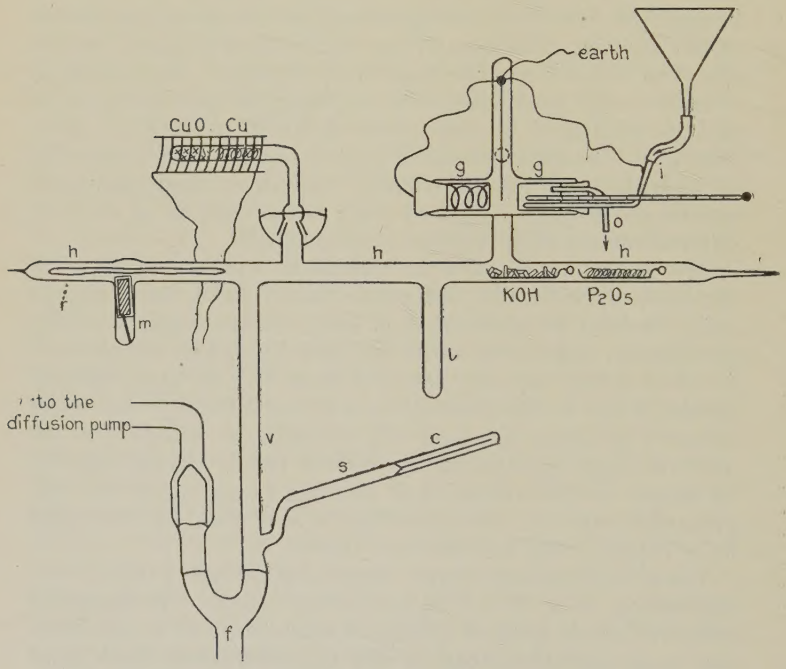
These experiments were unsuccessful, my preparations containing only 17 to 24 per cent. radon. It appeared evident that, in spite of a detailed description of the purification technique contained in the quoted papers, there were still some doubtful points left, and I decided therefore to study the details of the purification process.

As mentioned before, the pressure of radon is generally very small, and I have endeavoured, therefore, to build my purification apparatus according to the principles of high vacuum technique, and, in particular, to avoid the use of the transfer pump.

* Ramsay and Gray, Trans. Chem. Soc. xcv. p. 1073 (1909).
† Debierne, *C. R.* p. 1264 (1909).
‡ Rutherford, Phil. Mag. xvi. p. 300 (1908).

The purification apparatus based on these considerations is shown in fig. 1. Its essential part is a horizontal glass tube *h* of abont 10 mm. diameter, ab. 40 cm. long, which could be evacuated through the fork *f* by means of a diffusion pump backed by a Töpler pump. The gases pumped off during purification could be collected in a tube over mercury, which was useful for testing loss of radon and for avoiding radioactive contamination of the laboratory. To the vertical

Fig. 1.



Purification apparatus.

tube V of ab. 30 cm. long leading to the fork was sealed a small tilted side tube S extending into a calibrated capillary C, into which the purified radon could be compressed by means of mercury.

The tube *h* contained the purifying agents. KOH and P_2O_5 were introduced in glass boats. Copper oxide activated by heating to a high temperature with a few drops of palladium nitrate and copper gauze reduced by heating in a hydrogen stream were contained in a pyrex glass tube,

which communicated to the tube r by means of a ground oint surrounded with mercury.

Tube l is used for condensing radon in liquid air. GG is a calibrated Knudsen gauge of low sensitivity. Its moving part is an Al leaf of about 4μ thickness hanging between flat parallel surfaces. These surfaces form the ends of two vessels sealed into the tube g, which has the form of a double Dewar glass. The one vessel is closed by a cork provided with a thermometer and inlet and outlet tubes i and o. The inlet tube communicates to a funnel, and so the vessel can be filled alternatively with hot or room temperature water. In order to avoid electrostatic forces it was found sufficient to put a copper spiral in the empty vessel, a copper wire in the other vessel, and to connect spiral and wire with the leaf and the earth. The deflexion of the leaf is measured by a microscope with an eyepiece scale giving ·1 mm. per division. The sensibility is about 2 divisions for 1 bar when the temperature of water is changed from t, the room temperature, to $t+10°$. This gauge is very convenient for the region of pressures used, and the readings can be taken very quickly.

Radon is admitted into the apparatus in the following way. A tube of about 5 mm. diameter, drawn at one end into a thin-walled capillary, was filled with partly purified radon ; the total quantity of gas was ·1 to ·3 cm.^{3} at atmospheric pressure. This tube was introduced into the tube h so that the thin-walled part lay over the tube m, which contained a cylindrical piece of iron in a sealed glass cylinder. After thorough evacuation of the purification apparatus and its separation from the diffusion pump, the capillary was broken by approaching an excited electromagnet to the part of h just over the tube m.

In order to find out the best conditions for using this apparatus, different gases which might be supposed to form an impurity of radon were introduced, and operations exactly identical to those used in purification of radon performed.

If the purification is efficient, these gases ought to disappear and give, after introducing and compressing them into the capillary, a negligibly small volume.

The quantity of each gas was of the order of a few tenths of 1 cm.^{3} at atmospheric pressure. The investigated gases were : hydrogen, introduced by heating in a gas flame a palladium tube, not shown in the figure ; carbonic dioxide prepared by heating pure magnesium carbonate, and coal-gas, which formed an extreme case of impurity owing to the large amount of hydrocarbons and carbon monoxide

contained in it. The coal-gas was introduced through a transfer pump sealed between the Töpler and the diffusion pump.

The operations were performed in the following order :—

1. The apparatus was thoroughly exhausted, the Knudsen gauge baked out, and other parts bombarded by an electrodeless discharge. The final pressure indicated by the Knudsen gauge was of the order of the vapour pressure of mercury.

2. Communication with the diffusion pump was cut off by raising mercury in the fork.

3. The gas to be investigated was admitted in the way described above (in the case of radon the thin-walled tube was broken magnetically).

4. Copper oxide was brought to about 600° for $\frac{1}{2}$ hour.

5. Gas was allowed to stay in presence of reagents for a given time, one of the objects of the experiments being to find the shortest time necessary for an efficient purification.

6. Liquid air was put on tube *l*.

7. Uncondensed gases were pumped off by lowering mercury in the fork for a short time (ca. 10 secs.) and repeating this operation three or four times. The removal of these gases was considered as complete when the gauge showed a pressure of 2 bars, half of which at least was due to mercury vapour. The volume of the part into which condensable gases were to be transferred was about 2 cm.^{3}, so that at a pressure of 1 bar the amount of uncondensed gases contained in this part corresponded to ·002 mm.^{3} at atmospheric pressure—a very small quantity compared with the amount of radon usually dealt with.

8. Liquid air was taken off and the tube reheated to room temperature.

9. Condensed gases were distilled into tube S by wrapping it with cotton-wool soaked in liquid air. The tube S was allowed to communicate with the remaining apparatus for 5–10 minutes.

10. Mercury was raised in the tube V separating gas collected on S.

11. Cotton-wool was taken off and the tube warmed up.

12. Released gas was compressed by raising mercury still higher into the capillary, its volume and pressure determined in the usual way allowing for the capillary correction.

Hydrogen was tried first. Its disappearance was quick and practically complete, as was to be expected. But carbonic dioxide gave some unexpected results, which it is worth while to describe in detail, because its behaviour explains all the difficulty of obtaining a good purification of radon.

When pure CO_2 is admitted at an initial pressure of a few millimetres into the apparatus, its pressure, owing to absorption by the KOH, falls within 10–20 minutes to a fraction of a bar. If, however, we try to determine its residual amount by distilling the gas into the side tube and compressing it into the capillary, it will generally be found that its mass, measured by the product of volume and pressure, is many times greater than calculated. For instance, in one experiment I obtained, after 10 minutes' condensation, 1 mm.^{3} CO_2 under a pressure of 200 mm. Hg. ($pv = 250$ cm.^{3} × bar), while its original pressure in a volume of ab. 50 cm.^{3} was ·5 bar.

When expanding the compressed gas in the purification apparatus, its pressure drops instantaneously to a value somewhat above the original and seems to diminish slowly afterwards. If we repeat in equal successive intervals the determination of CO_2 by the capillary method, we shall find each time smaller values, but, as a rule, many hours are necessary before we get a "pv" of the order of 10 cm.^{3} × bar. When we remember that the pressure of ·1 curie radon in 10 cm.^{3} is ab. 6·5 bars, we realize at once that effects of this kind *may result in a complete failure of a purification experiment.*

The only possible explanation of this curious behaviour of CO_2 is that it is very strongly adsorbed by glass. During condensation gas is permanently given up by the glass walls, and the amount of it collected in the capillary in a given time depends on the rate of flow of CO_2 and its pressure in the purification apparatus. Experiments have shown that this amount increases in the first half hour nearly linearly with the time, which proves that the free pressure of CO_2, and consequently the quantity adsorbed, diminishes very slowly during the distillation. It has been found in one experiment that the quantity of distilling gas was about 20 cm.^{3} × bar per minute, the rate of flow through the tube being about 100 cm.^{3}/sec. as calculated from its dimensions.

It results that the pressure of CO_2 during distillation was about $3 . 10^{-3}$ bar. These figures illustrate well the importance of adsorption of CO_2 in glass and the difficulty of getting rid of it. It is interesting to give an approximate evaluation of the total amount adsorbed. This amount could be estimated to be about 2000 cm.^{3} × bar, *i. e.*, ab. $5 . 10^{16}$ molecule. The total area of the walls of the purification apparatus amounted to about 200 cm.^{2}, so that we get $2{\cdot}5 . 10^{14}$ molecules per cm.^{2} or 25 per cent. of the amount necessary to form a mono-molecular layer. The above figures are given, of course, only as an estimate. Their order of magnitude is, however, surprising. From Langmuir's data we infer that an adsorption layer of CO_2, equivalent to the one found in my experiment, exists on mica *at* $-80°$ *and at a pressure of* 172 *bars!* *

The adsorption effects on glass and on mica being of the same order of magnitude, we may safely deduce from Langmuir's experiments with mica at $-80°$, that the equilibrium pressure for the same adsorption layer on glass at room temperature would be superior to 172 bars. In my experiments the pressure during the distillation was $3 . 10^{-3}$ bar, and before distillation, ·5 bar.

The contradiction between mine and Langmuir's results is very striking. It is true that in Langmuir's experiments glass and mica were baked out completely and water-vapour kept off the adsorbing vessels, while in the experiments just described parts of the apparatus only could be heated to a really outgassing temperature, and some water-vapour, evolved by KOH and P_2O_5, was always present. But similar results, to be described more in detail in another paper, have been obtained with an apparatus which could be completely outgassed. It seems that the difference of results is rather due to the sensitivity of my method for detecting adsorption layers which give a very low equilibrium pressure.

It has been found recently † that glass treated by acids does not possess a smooth surface, so that its adsorbing area is certainly many times greater than calculated from its dimensions. Moreover, the corrosion products formed by the action of acids on glass form capillary spaces, and, therefore, the exchanges between the gas and the adsorbed layer take place more slowly than would be expected in a simple adsorption phenomenon. The behaviour of CO_2 on glass can be easily explained on these assumptions. The sharp

* Langmuir, Journ. Am. Chem. Soc. xl. p. 1361 (1931).

† Fraser, Patrick, & Smith, Journ. Phys. Chem. xxxi. p. 897 (1927).

fall of pressure when distillation sets in (from ·5 to ·003 bar) shows that gas is given up very slowly by the adsorbing layer, so that probably the rate of outgassing is given by the rate of escape of CO_2 from the complicated capillary interstices on the glass surface. The partial irreversibility of the effects observed when the CO_2 is expanded into the original volume is another proof that the effects cannot be due to an adsorption on a smooth surface, in which case a perfect reversibility is to be expected.

It would certainly be interesting to repeat these experiments with freshly blown glass, carefully kept out of contact with water-vapour, for in this case, according to the work of Fraser, Patrick, and Smith, the surface of the glass ought to be smooth.

This would be, of course, impossible in the purification work, owing to the formation of large quantities of water-vapour by the effect of CuO on hydrogen. It seems that a radical way of getting rid of the disturbing adsorption effects would be to keep the whole apparatus at a high temperature, except the part containing KOH and P_2O_5. This, however, would make the experimental arrangement very complicated.

It is much simpler and quite sufficient for purposes of purification to leave the gaseous mixture for a long time in contact with KOH. It will be remembered that this solution was found long ago by Rutherford, who stated that 24 hours were necessary for KOH to absorb the last traces of CO_2.

In this case KOH is acting like a pump which is extracting CO_2 from the glass walls. As in the above condensation experiments, the rate of this extraction is really the rate of what could be called diffusion of CO_2 through the adsorbing products of glass corrosion, and a period of the order of one day is just what would be expected for a process of this kind.

In comparing KOH to a pump for CO_2 it is important to say a few words about its "efficiency" and its "limiting pressure."

Theoretically the limiting pressure is the dissociation pressure of K_2CO_3, which is negligibly small, and the efficiency, *i.e.* the number of CO_2 molecules absorbed per unit time, is of the order of $\frac{1}{4}$ NΩS, where S is the total area of KOH, N is the number of molecules per 1 cm.^{3}, and Ω the mean velocity of CO_2 molecules. But this is true only for a fresh KOH surface. If the "area" is to be taken in the macroscopic sense it would be generally of the order of

10 cm^2., and a continuous layer of CO_3K_2 would be formed on it after absorption of 10^{16} molecules (·3 mm.^{3} at atmospheric pressure). The amount of CO_2 introduced with radon is certainly many times more than this. We are led to expect that the process of removal of CO_2 would be very quick at first, being given by the rate of collisions of CO_2 molecules with KOH, and very slow at the end, being given by the rate of diffusion of CO_3K_2 into KOH. This expectation is supported not only by my experiments, where it was found that after a sharp fall in pressure below 1 bar the further fall went on very slowly, but also by Debierne, who states that "apparently chemical reactions are extremely slow at very low pressures."

All the above considerations clearly point to the conclusion that it is impossible to obtain absolutely pure radon by use of chemical reagents only. All authors who have described the purification process state that the volume of radon immediately after compression into the capillary is generally greater than the one theoretically expected. The volume undergoes in most cases a marked contraction in the first few hours, remains afterwards stationary, and it is its final value which is assumed to be the volume of pure radon. These results will be discussed in another paper in connexion with my own results obtained by the same method. For the present it will be sufficient to say that the chemical method, at least in the form described in this paper, is not absolutely efficient in removing CO_2.

When working with a quantity of radon of the order of 50–100 millicuries, the amount of CO_2 found with radon after a carefully conducted experiment will be, in general, about 20 to 50 per cent. of the total quantity of gas.

The important question is to know if CO_2 is the only impurity left with radon (with the exception of traces of water-vapour and of mercury-vapour, the presence of which is immaterial in capillary tubes when gas is compressed at atmospheric pressure, and also of traces of uncondensed gases, mostly hydrogen, due to an incomplete evacuation). *A priori* it does not seem improbable that some heavier hydrocarbons would behave in a similar way.

As it would be very difficult to investigate all hydrocarbons, I performed some experiments with coal-gas, which contains them in a great quantity and variety. The result was that, with an initial volume of about 5 cm.^{3}, the volume immediately after oxidation by copper oxide was about ·1 mm.^{3}, but when gas was allowed to stay overnight with KOH this volume fell to about ·005 mm.^{3} (equal to the

volume of 8 millicuries of radon). As hydrocarbons are not absorbed by KOH this behaviour is obviously to be ascribed to the presence of CO_2 formed by the combustion of the coal-gas. We can conclude with some certainty that, in the method described in this paper, the only permanent gas which is concentrated with radon by use of liquid air is carbon dioxide.

[This work was performed during the years 1925/1926 and 1926/1927 in the Cavendish Laboratory.

It is a great pleasure for me to express my best thanks to Sir Ernest Rutherford for his kindness in receiving me in the Cavendish Laboratory, in placing at my disposal the large quantities of radon, and in showing a permanent interest in the progress of my work.

I am grateful to Dr. Chadwick for his help and interest.

I thank Mr. Crowe for the preparation of sources. My stay in England was made possible by a fellowship granted by the International Education Board. I wish to express my thanks to this Board.]

CIV. *Ranges of the Alpha-Particles of Uranium I. and II* *. *By* George C. Laurence, *Department of Physics, Dalhousie University, Halifax, Canada* †.

I. *Introduction.*

NEARLY all the ranges of the alpha-particles emitted by the radioactive elements have now been measured accurately. The values, however, for uranium I., uranium II., and thorium may be considerably in error due to experimental difficulties resulting from their low activity. An accurate knowledge of the ranges of the latter elements is desirable for several reasons. Among these is the establishment of the validity of the Geiger and Nuttall Curve for elements of small decay constant. Apparent disagreement, moreover, between the ranges, as measured by Geiger and Nuttall in 1912 ‡, and as calculated from pleochroic

* Carried out with the aid of a National Research Council of Canada Bursary.

† Communicated by Prof. G. H. Henderson, Ph.D.

‡ H. Geiger and J. M. Nuttall, Phil. Mag. xxiii. p. 439 (1912).

halo data *, has led to a suggestion that there has been a gradual change in their ranges and decay constants throughout geological time.

A new determination of the ranges of uranium I. and II. has therefore been made, using the Wilson Chamber Method, which appeared likely to yield higher accuracy than the usual ionization and scintillation methods. The method consists essentially of photographing the tracks produced by the alpha-particles in a Wilson expansion chamber and measuring the photographs. The extremely small activity of the radioactive material made it necessary to make special modifications in the method, namely, to use a source of large area, to open the camera shutter by hand, and to operate the chamber without shutters to cut off the radiation before the completion of expansions.

II. *Apparatus.*

The Wilson expansion chamber had a diameter of 6 cm. and a maximum depth of 1 cm. Its piston was operated by a lever, cam, and spring mechanism, so arranged that by turning a crank the piston was raised slowly and then quickly lowered, producing a practically adiabatic expansion. A fine bore mercury manometer connected to it provided for the measurement of the pressure inside, and a thermometer inserted between projecting flanges on the chamber indicated the temperature. The usual gelatin film kept the air in the chamber moist and served as an electrode for the field of 200 volts across the chamber.

The chamber was lighted from the side by a 10-ampere d.c. arc, the light from it passing through condensing lenses, and water to absorb heat radiation.

The camera had an f. 4·5 lens of focal length 7·5 cm., and was mounted 20 cm. above the chamber. Kodak Super-Speed Cine Film was used, being carried on reels in a box detachable from the back of the camera. Exposures of ·4 to ·6 sec. were used.

Although an electric device to operate the shutter automatically at the end of each expansion was made, it was found that the shutter could be operated by hand before the tracks diffused enough to affect results. Considerable saving of time and film was thus effected, as, on the average, only one expansion in eighty produced a track suitable for photographing.

* J. Joly, Trans. Roy. Soc. A, 551, p. 51 (1917); B. Gudden, *Zs. f. Phys.* xxvi. p. 110 (1924).

III. *Source.*

The radioactive source had to be such as to provide as many tracks as possible and at the same time cause little absorption of the alpha-particles. It had, therefore, to be of large area and very thin. The preparation of this source offered some difficulty, but it was finally accomplished by subliming uranium vapour on strips of mica. Small lumps of metallic uranium, supported on the ends of tungsten wires, formed the electrodes of an electric arc. The arc was struck in a pressure of a few millimetres of air, which was just sufficient gas to maintain it. The vaporized uranium deposited in a thin uniform film on the mica strips which were placed around the arc. A current of 10 amperes for a minute produced a film of the required thickness, 8 mg. per sq. cm., equivalent in absorption to 2 mm. of air. A strip thus prepared, 10 cm. long by ·7 cm. wide, fastened to the side wall of the chamber with soft wax, served as the uranium source. About one-third of the glass wall remained bare to admit the light to illuminate the tracks.

The size of the source practically prohibited the use of shields and shutters to cut off the radiation before the expansions were complete. This difficulty was overcome by making the expansions very rapid. Thus more than 98 per cent. of the total number of tracks seen are formed at constant density after the expansion is complete and while the chamber is warming up to the temperature above which the vapour will no longer condense on the paths of the alpha-particles. The remaining, less than 2 per cent., which occur at slightly lower pressures, introduce a quite negligible error in the result. The fraction of the tracks which occur before the completion of expansion was here calculated from an approximate comparison of the time interval during which the expansions continue beyond the minimum value necessary to produce condensation on the tracks with the time it takes the average temperature in the chamber to rise until the condensation will no longer occur.

IV. *Preliminary Experiments with Polonium.*

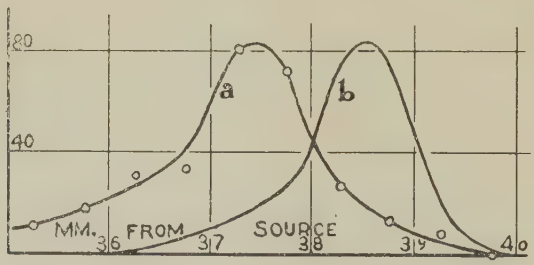
Thus modified, the method was applied to the alpha-particles of polonium as a check. For a source, small pieces of a glass tube which formerly contained radium emanation were used, being stuck to the walls of the chamber with wax. The photographs of the tracks were measured, corrected for the magnification of the camera, temperature, air and vapour pressure, and the obliquity of the tracks, as will

be described later. The range of polonium at 15° C. and 760 mm. was thus found to be 3·84 cm. The best recent values are :

Mlle I. Curie *, 3·92 cm.
H. Geiger †, 3·925 cm.

The fact that our value is somewhat smaller than these is probably due to the penetration of the radioactive material into the glass by the recoil of Rn, RaA, and RaC'. A rough application of the correction for finite thickness of source (see subsequent section), to correct for the resulting absorption, brings the range up to 3·90 cm., in good agreement with the accepted value. The results of 164 tracks are shown in fig. 1, curve *a*, where the number of polonium tracks of length between ·5 mm. less than and ·5 mm. more

Fig. 1.



than the abcissa is plotted. Mlle Curie's curve is given for comparison (curve b). The fact that the straggling shown in our curve is not very much greater than in hers, obtained under the most favourable conditions, justified proceeding with the method.

V. *Uranium Measurements.*

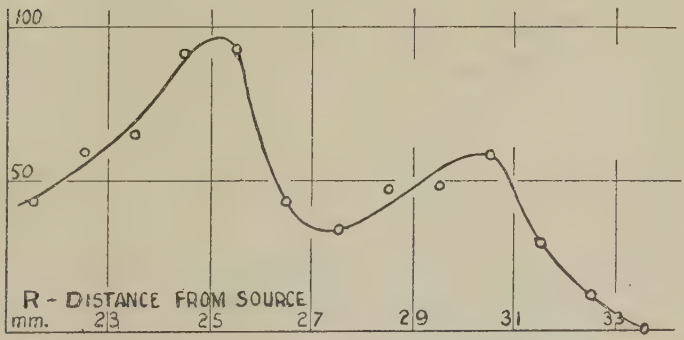
The experimental method was as follows: holding the cable shutter release in one hand and turning the crank which operates the piston with the other, the chamber was watched for the appearance of a cloud track. When a track was seen the camera was immediately snapped. The stop-cock connecting the manometer with the chamber was then opened, air-pressure and temperature read and recorded. The stop-cock was then closed and the film-reel given a turn

* I. Curie, *Ann. de Phys.* iii. p. 299 (1925).
† H. Geiger, *Zs. f. Phys.* viii. p. 45 (1922).

ready for the next exposure. About 1620 photographs of uranium tracks were taken. This required over 120,000 expansions. Poor photographs, and photographs of tracks whose length was less than 1·5 cm. or whose ends were indistinct, were discarded. The remaining 900 photographs of tracks were measured with the aid of a transparent scale and a small magnifying glass, and the lengths so obtained were multiplied by the magnification of the camera, which was determined by photographing lengths of fine glass tubing placed in the chamber. As the length of a path varies inversely as the density and the square root of the atomic weight of the gas, it was corrected for temperature, air and vapour pressure, to obtain the path-length in dry air at standard conditions.

The lengths of the tracks are plotted in figs. 2 and 3. In fig. 2 the ordinates represent the number of tracks having

Fig. 2.



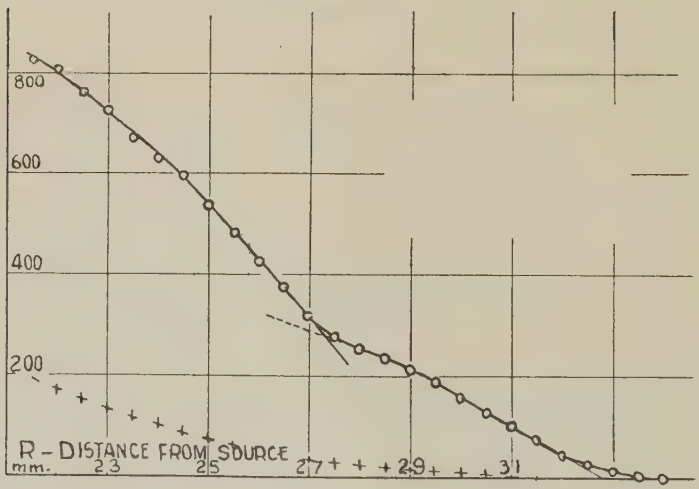
a length lying between ·05 cm. less than and 0·5 cm. more than the length indicated by the abscissa. In fig. 3 the ordinates represent the number of tracks of length greater than the abscissa. Only one track of length greater than 3·40 cm. was obtained. Its length, 3·67 cm., indicated it to be due to polonium contamination and it was therefore disregarded. The corrections discussed in § VI. and § VII. were applied in plotting fig. 2 and fig. 3.

It will be seen that Curve 3 falls off rapidly to zero as the end of the range of uranium II. is reached. The range of uranium II. is obtained in the customary manner by extending the slope at the end of the curve to intersect the range axis. Superimposed on the curve representing the uranium II. tracks is another similar curve corresponding

to the shorter range uranium I. Producing the slope at the end of this curve to intersect the uranium II. curve extrapolated back (along the dotted curve in the figure) gave the range of uranium I.

While the photographs were being taken the source was changed, the apparatus taken apart and cleaned, and the gelatin layer renewed several times, and the pressure varied from 570 to 770 mm. of mercury. That such changes had practically no effect on the results was shown by dividing the tracks into groups representing different conditions and comparing the corresponding curves. These resembled each other as well as would be expected with such small groups of tracks.

Fig. 3.



VI. *Correction for Absorption by Source.*

The range as determined in the manner described above depends slightly on the absorption of the radiation by the source itself. As it was not practical, because of the small activity of uranium, to use a source so thin as to cause negligible absorption, the effect of the absorption on the range will now be calculated and added as a correction to the range obtained from the curve.

Bohr * and Flamm † have shown theoretically, and

* Bohr, Phil. Mag. xxv. p. 10 (1913); xxx. p. 581 (1915).
† Flamm, *Wien. Ber.* cxxiii. p. 1393 (1914); cxxiv. p. 397 (1915).

I. Curie *, Mercier †, Meitner and Freitag ‡, and others have verified experimentally, that the lengths of the tracks emanating from a very thin source are distributed about a mean value R according to the error law. That is, the fraction dz of the total number of tracks which has a range differing from this mean value by a distance $+x$ is given by

$$dz = \frac{1}{a\sqrt{\pi}} e^{-\frac{x^2}{a^2}} dx, \quad . \quad \text{(Fig. 4, Curve } a\text{)}$$

where a is a parameter determining the extent of the straggling. The fraction of the tracks which are longer than $R+x$ is therefore

$$z = \frac{1}{a\sqrt{\pi}} \int_x^\infty e^{-\frac{x^2}{a^2}} dx. \quad . \quad \text{(Fig. 5, Curve } a\text{)}$$

Since we are using a source of finite thickness, equivalent in absorption to m cm. of air, the measured ranges of those particles which come from a layer of the source at a depth v below the surface and of thickness dv (where v is measured in equivalent cms. of air) are shortened by a distance v. The fraction of the tracks having a range longer than $R+x$ is therefore

$$\frac{dv}{m} \cdot \frac{1}{a\sqrt{\pi}} e^{-\frac{(x+v)^2}{a^2}} dx.$$

v is so small that the change in a resulting from it may be neglected. So the fraction of the total number of tracks having a measured range greater than $R+x$ is

$$dz_1 = \frac{dx}{ma\sqrt{\pi}} \int_0^m e^{-\frac{(x+v)^2}{a^2}} dv,$$

$$= \frac{dx}{ma\sqrt{\pi}} \int_x^{x+m} e^{-\frac{x^2}{a^2}} dx. \quad \text{(Fig. 4, Curve } b\text{)}$$

Hence the fraction of the number of tracks whose measured length is greater than $R+x$ is

$$z_1 = \frac{1}{ma\sqrt{\pi}} \int_0^\infty dx \int_x^{x+m} e^{-\frac{x^2}{a^2}} dx.$$

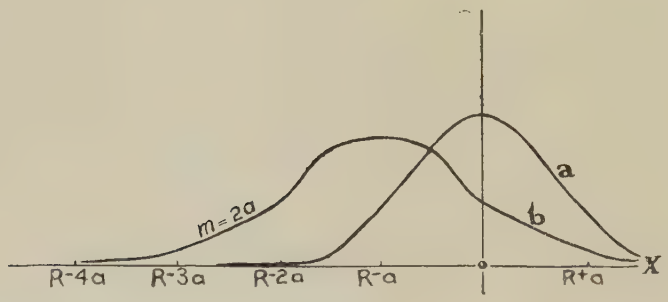
* I. Curie, *Ann. de Phys.* iii. p. 299 (1925).
† I. Curie and P. Mercier, *Journ. de Phys.* (6), vii. p. 289 (1926).
‡ L. Meitner and K. Freitag, *Zs. f. Phys.* xxxvii. p. 481 (1926).

This may be integrated by parts, yielding

$$z_1 = \frac{1}{ma\sqrt{\pi}}\Big[-x\int_x^{x+m} e^{-\frac{x^2}{a^2}}\,dx + m\int_{x+m}^{\infty} e^{-\frac{x^2}{a^2}}\,dx + \frac{a^2}{2}\left(e^{-\frac{x^2}{a^2}} - e^{-\frac{(x+m)^2}{a^2}}\right)\Big]. \quad \text{(Fig. 5, Curve } b\text{)}$$

It is evident that if the tangents to the points of inflexion d and f (fig. 5) are produced down to intersect the range axis in the manner usual in determining the ranges, they will do so in two separate points, g and h. To obtain the ranges for a very thin source the distance gh must therefore be added to the measured range.

Fig. 4.



The point of inflexion is found by equating the second derivative of z_1 to zero in the usual way. This gives $x = -\frac{1}{2}m$, which, when substituted in the equation of the curve, gives $z_1 = \frac{1}{2}$.

The slope at the tangent at this point is

$$\frac{dz_1}{dx} = \frac{1}{ma\sqrt{\pi}}\int_{-\frac{1}{2}m}^{+\frac{1}{2}m} e^{-\frac{x^2}{a^2}}\,dx = \frac{1}{m}\operatorname{erf}\frac{m}{2a},$$

where $\operatorname{erf}\dfrac{m}{2a}$ represents the expression

$$\frac{2}{\sqrt{\pi}}\int_0^{\frac{m}{2a}} e^{-y^2}\,dy.$$

Hence the intersection of the tangent with the X-axis is

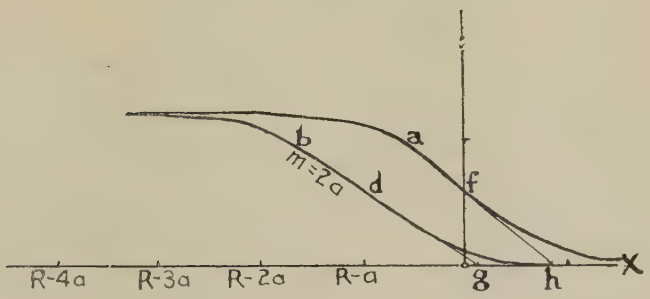
$$z_1' = x - \left(z_1 \Big/ \frac{dz_1}{dx}\right) = -\tfrac{1}{2}m + m/(2\operatorname{erf}(m/2a)).$$

When m approaches 0, as in Curve 5*a*, this expression reduces to $z_1' = \frac{1}{2}a\sqrt{\pi}$. So the required distance between the intercepts g and h is

$$\tfrac{1}{2}a\sqrt{\pi} + \tfrac{1}{2}m - m/(2\,\mathrm{erf}\,(m/2a)). \quad . \quad . \quad . \quad (1)$$

As m increases, the value of this expression approaches $\frac{1}{2}a\sqrt{\pi}$ and differs very little from $\frac{1}{2}a\sqrt{\pi}$ for m greater than $2a$, and therefore need be known very accurately. This does not imply that m might just as well be quite large. Increasing it has the effect of flattening the slope of the curve and thereby making its intercept more difficult to determine accurately. It also causes the slopes corresponding

Fig. 5.



to the two uraniums to overlap, making them difficult to distinguish.

Putting in the value of m and the value of a for the two uraniums, the corrections are calculated to be +·040 cm. for uranium I. and +·045 cm. for uranium II.

VII. *Other Corrections.*

Small corrections for the apparent shortening of the rays due to their obliquity to the photographic film must be added to the ranges. These corrections are derived as follows:—

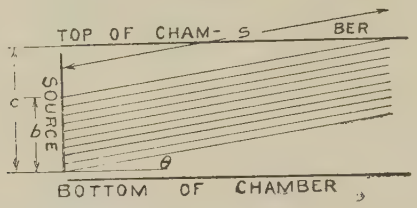
Let s be the average length of the tracks and c the depth of the chamber. Of the tracks whose angle of inclination to the horizontal is θ, only those coming from a strip of width $b = c - s\sin\theta$ along the bottom of the source will escape hitting the top or bottom of the chamber before the end of their path. Their number is therefore proportional to $c - s\sin\theta$. Their apparent length is $s\cos\theta$. See fig. 6.

Their average length is

$$\frac{2\int_0^{\sin^{-1}c/s}(c-s\sin\theta)\,s\cos\theta\,d\theta}{2\int_0^{\sin^{-1}c/s}(c-s\sin\theta)\,d\theta}.$$

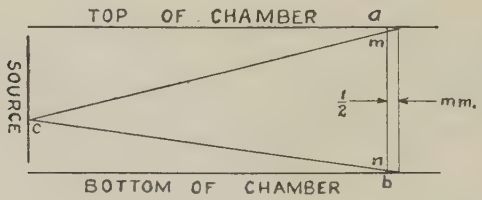
Solving and filling in the numerical values it is found that the ranges of uranium I. and II. are shortened by ·016 cm. and ·018 cm. respectively.

Fig. 6.



About 20 per cent. of the tracks have struck the top or bottom of the chamber. Their distribution is such, however, that they produce negligible effect on the range as determined above. Starting at 2·1 cm. from the source, we see from fig. 3 that there are 802 particles which travel farther than this. These all pass between a and b, fig. 7. Of this number,

Fig. 7.



only those passing between a and m and between n and b strike the top or bottom in the next half millimetre. Their number is proportional to the angle subtended at c, and since the angles are small, the fraction of the total number which strike the walls in the next half millimetre is $(am+nb)/ab$.

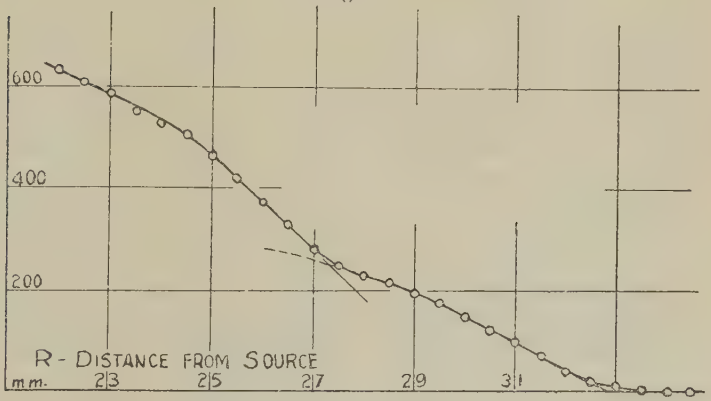
Continuing in this manner the number which strike the walls in each half millimetre is determined, and from these figures the dotted curve of fig. 3 is obtained, indicating the number of tracks of range greater than the abscissa which hit the top or bottom. Subtracting the ordinates of thi curve from those of the solid line curve we get the curve o

fig. 8, showing the number of the tracks which have not hit the walls that are longer than the abscissa. If this curve is used in determining the ranges, the intercepts are found to fall on the same points as those of fig. 3 within the possible accuracy of plotting.

It may be noticed that in fig. 8 there are more uranium I. than uranium II. tracks. This is due to the shape of the chamber ; short range particles have a larger solid angle in which they may be projected without hitting the walls.

The heating of the chamber by the radiation from the arc light was investigated by using the chamber and manometer as an air thermometer. Comparisons of the temperature measured in this manner with the reading of the thermometer

Fig. 8.



showed that the temperature of the chamber averaged ·5 degree above the thermometer during the time taken for a series of expansions. The corresponding correction of ·005 cm. was therefore subtracted from the ranges.

Possible sources of error not considered above are : the obliquity of the rays of light from the ends of the tracks to the axis of the lens, errors in measuring pressure, and in measuring the tracks themselves. These probably total less than ·02 cm. for most of the tracks.

VIII. *Results.*

Applying the corrections discussed above the ranges in dry air at 150° C. and 760 mm. of mercury are

Uranium I..... 2·73 cm.
Uranium II. ..... 3·28 cm.

The error in these is probably less than 1 per cent.

Applying Geiger and Nuttall's law to the range 3·28 cm. gives for the decay constant of uranium II., which has never been measured,

$$1{\cdot}7 \times 10^{-12} \text{ reciprocal seconds,}$$

making the half-life 13,000 years.

The range of uranium I. is about intermediate between Geiger and Nuttall's value and Gudden's value obtained from pleochroic halo data. Assuming that it has a half-life of $4{\cdot}67 \times 10^9$ years, the range of uranium I. calculated from the Geiger and Nuttall relation is 2·67 cm., slightly smaller than the present value. The range of uranium II. is considerably longer than the older values.

In a preliminary report on this work *, based on less data, comprising 370 tracks, the ranges were given as 2·72 and 3·29 cm. respectively, differing very little from the final values.

IX. *Summary.*

The ranges of the alpha-particles of uranium I. and II. were determined by the Wilson Cloud Chamber Method, with modifications made necessary by the small activity of the radioactive material.

The method was satisfactorily checked by its application to the range of polonium.

The ranges at 150° C. and 760 mm. of mercury were found to be

Uranium I.	2·73
Uranium II.	3·28

with a probable error of less than 1 per cent. From the range of uranium II. its decay constant was calculated to be $1{\cdot}7 \times 10^{-12}$ sec^{-1}, or a half-life of 13,000 years.

The uranium metal for the source was kindly furnished by Dr. G. M. J. MacKay, of the General Electric Co., Schenectady, N.Y.

The author is gratefully indebted to Dr. G. H. Henderson for suggesting this problem and for his encouragement and advice. Mr. R. H. Fowler very kindly checked the calculations contained in Section VI., and the adoption of his suggestions added considerably to the clearness of that section.

* G. C. Laurence, Trans. Nova Scotia Inst. of Sci. xvii. p. 103 (1927).

CV. *On the Primary Dark Space of a Geissler Discharge.*

By K. G. Emeléus, *M.A., Ph.D., Lecturer in Physics, and* Nora M. Carmichael, *B.Sc., Musgrave Demonstrator, Queen's University of Belfast* *.

1. *Introduction.*

THE cathode dark space of a glow discharge, although only relatively non-luminous, is actually separated from the cathode in some instances by a thinner intensely dark layer. This "primary dark space" was first noticed by F. W. Aston on an aluminium cathode in helium, hydrogen, and mixtures of helium with oxygen [1], and the same appearance was subsequently found by Aston and Watson to be presented by discharges through all the inert gases, being clearest in helium and xenon [2]. Kossel made a detailed study of the primary dark space on an electrode of potassium in helium [3], whilst Holst and Oosterhuis examined certain features of it in neon [4]. The present writers have observed it on a nickel electrode with argon containing some hydrogen. It does not appear to have been recorded up to the present in gases other than those mentioned.

Aston also found that striæ were present beyond the first dark space in helium [1]; these became less distinct as the negative glow was approached, but the differences in potential between them were approximately constant, so far as could be judged from rough estimates of the electric intensity. In neon, the primary dark space replaces the first of the dark negative striæ characteristic of the transition region between the normal glow discharge and simple ionization by collision, when the current is increased [4]. The difference in potential between the negative striæ is about the ionization potential of neon [4], and the number of ions in the luminous parts is almost doubled at each fresh striation towards the anode [5]. By analogy, the fall of potential across the primary dark space should be the ionization potential of the gas, but this cannot be verified from the distribution of the electric field, which is unknown for the conditions under which the primary dark space can be seen. These are not much different from those occurring with a normal cathode fall of potential, for which a theory has been given by K. T. Compton and Morse [6], but this again cannot be applied with certainty to the immediate neighbourhood of the cathode.

* Communicated by Prof. W. B. Morton, M.A.

A theory of this dark space was proposed by Aston [1], in which electrons from the cathode were supposed to move outwards to the negative glow, but to produce no visible effect until they had sufficient energy to ionize. The presence of striæ is an immediate consequence of this. It was shown subsequently by Güntherschulze [7] that it is also possible to explain in this way the apparent absence of the primary dark space in other gases, since, if the distribution of electric intensity found from the Stark effect for a strongly abnormal cathode fall is taken as an approximation to the state of affairs near the normal cathode fall, an electron starting at rest from the cathode would first produce radiation at a distance too small to be observed directly. The initial velocities of the electrons are probably small compared with the velocities required for ionization of the gases in question.

The experiments of Kossel, on the other hand, are not in complete agreement with this view. In helium, the main cathode dark space is blue-green, and the positive boundary of the primary dark space has a red rim. A closely similar light-structure can be produced within a hollow cathode built of mutually insulated sections, whose outer gauze surface is the main cathode of an ordinary glow discharge. The red rim can only be produced internally by an auxiliary electron-accelerating potential of not less than 21 volts. This is very close to a resonance potential of helium, which Kossel therefore concluded was the difference of potential between the faces. The energy of the electrons employed may, however, have been somewhat greater, since it had been shown that under somewhat similar conditions in hydrogen they left the cathode with initial energies equivalent to a maximum of about 2 volts, which has here to be diminished by the unknown work-function of the emitting surface. Moreover, the positive column of the main discharge was striated, which indicates that, although mercury was absent, other impurities may have been present, so that primary excitation of helium could have produced ionization by collisions of the second kind. In addition, the phenomena when hydrogen was used were less simple, and can be accounted for better on the ideas elaborated in § 2. However, even if Kossel's conclusion is correct, the general theory of the following section is not affected substantially, since the resonance potentials vary in much the same way as the ionization potentials.

It is not certain, nevertheless, that the relatively sharp outer boundary of the primary dark space is entirely due to the fact that the electrons lose practically no energy

until they make inelastic collisions. A cushion of light to the positive side of the primary dark space—the "cathode glow"*—often persists even when the primary dark space cannot be detected, and exhibits certain features which seem to differentiate it from the remainder of the cathode dark space. The most obvious of these are :—

(1) With strongly abnormal cathode fall, if not under all circumstances, some sections of it are electrically neutral or negative [8, 9].

(2) In hydrogen and oxygen, part of its light is due to positive rays [10].

(3) It is little affected by magnetic fields.

Experiments are in progress here on the characteristic curves of a collector in this part of the tube, and on the light from it, which it is hoped will give further information on this point, but it appears that the cathode glow is more nearly like the negative glow than is that part of the cathode dark space between the two glows. In the present paper, we propose to examine the consequences of supposing that the primary dark space is a positive ion sheath of the type studied by Langmuir in connexion with the use of cold exploring electrodes [11]. On this view, the flow of positive ions between the cathode and cathode glow is limited, as indeed elsewhere in the cathode dark space, by the positive space-charge which they produce, but a contributory cause to the absence of radiation will be that which is active at the surface of a negatively charged exploring electrode, in this case the cathode of the main discharge, rather than a specific inhibitory effect of free electrons, such as has been suggested by J. J. Thomson [12]. A simple theory of this type has already been tried by Ryde for the whole of the cathode dark space [13]. If this theory is correct, all the lines of force ending at the cathode start on positive ions in the primary dark space, and there must be a negative space-charge in part of the cathode glow to act as an effective negative electrode for the main cathode dark space, in agreement with Brose's observations, as far as the later can legitimately be applied here [8, 9]. It may be significant that the outer rim of positive ion sheaths in regions of feeble ionization has an appearance very like the cathode glow, being markedly brighter than the main discharge, which is possibly partly due in both cases to a local accumulation of electrons repelled from the sheath.

* Referred to in German literature as "Erste Kathodenschicht."

The facts which have to be accounted for are [1] :—

(*a*) That the primary dark space appears in only a limited number of gases.

(*b*) That $i^{\frac{1}{2}}d$ is approximately constant, where i is the current density, and d the thickness of the primary dark space.

(*c*) That d is independent of the pressure of the gas.

(*d*) That Vd/D is constant for any one gas, where V is the cathode fall of potential, and D the thickness of the cathode dark space.

2. *Space-Charge Theory.*

The difficulties that have been encountered in attempts to form a theory of the cathode dark space, which arise chiefly from incomplete knowledge of the origin and paths of the cathode rays, are less important in the limited region now under consideration. In particular, the appearance of the primary dark space strongly suggests that ionization only occurs beyond its boundary, whilst relatively few collisions are made by electrons and ions in traversing it. The contribution of the electrons to the space-charge in the primary dark space will be neglected, but their contribution (i_e) to the total current density (i) must be taken into account. If i_p is the current density of positive ions,

$$i_e + i_p = i. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The maximum thickness of the primary dark space is about 0·1 cm., and the pressures at which it can be seen are of the order of 1 mm. Hg, so that the number of collisions made by an ion in traversing it will usually be decidedly less than 10. Their effect will be neglected, and Langmuir's solution of space-charge limited conduction for a plane electrode used [14]. This takes the form

$$i_p = \frac{2{\cdot}34\ 10^{-6}\ V_i^{3/2}\{1+0{\cdot}025(T/V_i)^{\frac{1}{2}}\}}{\sqrt{1834\,M}\ d^2} \quad . \quad . \quad . \quad (2)$$

where V_i is the ionization potential of the gas (§ 1) and M is the molecular weight of the positive ions. The numerical constants correspond to current densities in amps./cm.^{2} potentials in volts, and distances in cms. With sheaths of comparable thickness, it has been found that the most consistent results are obtained if the effects of collisions are completely ignored [15]. There is uncertainty as to the value of T, the temperature of the positive ions when they enter the sheath ; Aston has given reasons for supposing that most

of the positive ions at low values of the cathode fall of potential should reach the neighbourhood of the cathode with approximately the energy obtained since the last collision with a gas-molecule [16], but the electric field at the outer boundary of the primary dark space is unknown. If, however, the correcting factor in equation (2) is taken to be approximately constant, the formula contains the experimental relation (*b*) between current density *i* and thickness *d*, on the additional plausible assumption that the relative contributions of i_e and i_p to *i* are independent of the exact value of the latter. The fact that *d* is independent of pressure (*c*) is implicit in the assumption that the effect of collisions can be neglected.

The connexion between the thickness *d* and the nature of the gas is more complicated. Equation (2) shows that *d* is inversely proportional to $M^{\frac{1}{4}}$, so that hydrogen, where the mass of the positive carriers may be $1(H^+)$, $2(H_2^+)$ or $3(H_3^+)$, and helium, where it is 4, are the only two substances specially favoured by this factor. The distance *d* is also proportional to $V_i^{\frac{3}{4}}$, if the factor in brackets is neglected, which should single out from other gases helium, with an ionization potential of 24·6 volts, and neon, with one of 21·5 volts. Measurement of *d* in the case of neon is also facilitated by the peculiar ease with which optical phenomena can be seen in discharges through it, whilst the same is probably true of xenon, and to a less extent of argon and krypton.

These considerations alone are, however, inadequate to account completely for the failure of the primary dark space to appear in other gases, to do which the magnitude of i_p, equation (2), must be taken into account. The total current density across the primary dark space is the same as that across the cathode dark space, so that i_p enters into the equation as an empirical quantity dependent on *i*, which in turn has to be found by experiment in each case. The general nature of the variation of *i* from one gas to another will be seen from Table I., taken from Güntherschulze's data for a cooled platinum cathode [17], i_n being the normal density at a pressure of 1 mm. Hg.

It will be seen that the current densities are smallest for the first four gases, and since *d* is inversely proportional to $i^{\frac{1}{2}}$ (*b*), this factor, taken in conjunction with those already mentioned, can be taken to show that *d* should be particularly large in helium, neon, and hydrogen. The differences between the various gases will be less at lower pressures, since i_n is proportional to the square of the pressure, but the

primary dark space is then more diffuse and difficult to detect. Argon should be more comparable with the polyatomic gases so far as the data of Table I. go.

Table I.

Gas.	He.	Ne.	A.	H_2.	O_2.	N_2.
l_n mA/cm.^{2}	0·01	0·02	0·14	0·09	0·55	0·38
l_p mA/cm.^{2}	0·7	0·25	0·1	0·6	0·14	0·16
D_n cm.	1·66	0·77	0·36	0·90	0·31	0·42

Krypton and xenon have been examined separately by Güntherschulze [18], and the normal current densities for these gases, obtained with a massive iron cathode, are shown in Table II. Both values of i_n are small, which will partly compensate for their large atomic weights.

Table II.

Gas.	Kr.	Xe.
l_n mA/cm.^{2}	0·04	0·02
l_p mA/cm.^{2}	0·05	0·03
D_n cm.	2·6	2·3

An exact quantitative test of equation (2) does not appear to be possible at present, both because of incomplete data in the literature on the primary dark space, and because of uncertainty as to the value of the bracketed factor. For the purpose of calculation, we shall assume that the latter has a constant value of 2, which is about what could be expected from Aston's analysis [16]. The current densities of positive ions against i_p in Tables I. and II. have been obtained in this way, and correspond to a primary dark space 0·1 cm. in thickness. In the case of nitrogen, where the positive ions are either N^+ or N_2^+, with masses of 14 or

28, a mean value has been taken. A similar procedure has been adopted with oxygen. For hydrogen, M has been taken to be 1·5. The values of V_i for the diatomic molecules have been used.

For the last two gases of Table I. and argon, i_n and i_p are of the same order, the former being the larger of the two, in general agreement with the facts that the positive ions transport a considerable fraction of the current to the cathode, and that for these gases d is certainly less than 0·1 cm. The agreement in Table II. is closer than could be expected, as there is great latitude in the choice of current densities. For hydrogen, i_n is definitely less than i_p, which might be explained, following Kossel, as due to the presence of mercury, which would lower the value of $V^{3/2}$ from about 64 to 36. In addition, no special precautions were taken to cool the cathode in Aston's experiments, and a rise in temperature has been shown to increase the value of the normal current density. It is unlikely, however, that these considerations explain the large values of the ratio i_p/i_n found for helium and neon, or that it is due to incomplete electrostatic shielding of the cathode by the primary dark space in these gases, and not in others. We would tentatively suggest that some such action as the following occurs.

If the current of positive ions is greater than the total current, a current of electrons must be flowing across the sheath against the electric field. This could take place either because of diffusion in a concentration gradient, or more probably because of the presence in the cathode glow of swift electrons moving in more or less random directions, and able to penetrate the sheath. We do not wish to lay stress on this point, because of the absence of exact data in support of it, but such electrons might give the secondary emission of electrons from the cathode which is usually attributed to impact of positive ions or a photoelectric effect, and so bring the discharge phenomena in line with the absence of secondary emission from outgassed electrodes bombarded with slow positive ions [19]. It would also partly explain why so great a fraction of the energy expended in the cathode fall space appears as heat at the cathode, by recombination of positive ions and electrons at the surface of the latter. It has been found by Mr. W. L. Brown and one of us (K. G. E.) in this laboratory, that electrons of the requisite energy are present in the negative glow, and certainly persist for some distance into the cathode dark space.

Given sufficient data, equation (2) gives ideally a means of finding the number of electrons which leave the cathode for

each positive ion received, by comparison of i with i, equation (1) [20].

The relation (d) was used by Aston to calculate the ionization potentials of hydrogen and helium. This leads to certain discrepancies which have been pointed out by Kossel, and in addition Vd/D increases with atomic weight amongst the inert gases, whereas V_i decreases. The present theory is not concerned with V and D, but Aston's relation can be shown to be in agreement with another semi-empirical formula that he established, viz., that if p denotes the pressure,

$$iD^3pV^{-2}=\text{const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

to a degree of approximation dependent on the gas used.

This can be regarded as derived from

$$Vpi^{-\frac{1}{2}}=\text{const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and

$$Dp=\text{const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

which are approximate forms of the empirical relations

$$V=\text{const.}+K_1 i\, p^{-1}, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and

$$D=K_2p^{-1}+K_3i^{-\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where K_1, K_2, K_3 are constants.

If p is eliminated between equations (4) and (5), on the grounds that the thickness of the primary dark space is independent of the pressure, we obtain,

$$VD^{-1}i^{-\frac{1}{2}}=\text{const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Both from the theory, equation (2), and experiment (b),

$$i^{\frac{1}{2}}d=\text{const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and hence from equations (8) and (9),

$$VdD^{-1}=\text{const.} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

It is impossible to predict the relative accuracy with which equations (3) and (10) would be expected to be true.

Somewhat similar conditions determine both d and D, and the values of the latter at normal cathode fall on iron, at a gas pressure of 1 mm. Hg., are shown against D_n in Tables I. and II. The data are taken from various publications of Güntherschulze [21]. Those gases showing a primary dark space have in general the greatest values of D_n.

3. *General Considerations.*

The genesis of the primary dark space from the low current striæ has been mentioned in § 1, and its intimate connexion with the latter is indicated by the presence of striæ in the cathode dark space in helium. There is evidence that the space-charge is negative between the luminous parts of a low current discharge, but there is instability in the transition to the normal glow, both in appearance and in the characteristic curve [4, 22] which may well be associated with a change in electrical conditions similar to that which accompanies "blueing" in a thermionic diode containing gas [23]. The disappearance of the striæ at higher current densities may be due to causes similar to those which govern the transition from a striated positive column to the unstriated form. When the current density is so high that the primary dark space itself is not visible, it need not, nevertheless, be actually absent. On the contrary, it may play an important part in the change from a glow to an arc, since there is strong evidence that the cathode of the latter is covered with a sheath of positive ions [24, 25], which may be generated from the primary dark space, rather than from the whole of the cathode dark space.

The discussion of § 2 is incomplete in several respects. In particular, it does not explain satisfactorily why a primary dark space is apparently absent in oxygen and nitrogen. It should be possible to detect it with more refined means of observation, if it is present, but very thin. It is possible that its presence is masked by radiation from excited molecules that have diffused into the sheath, although this is not the case with hydrogen, and with the mixtures of monatomic and diatomic gases in which it can be detected. Our main object has been to call attention to the fact that if the outer boundary of the primary dark space is at a definite potential relative to the cathode, then, on certain assumptions, space-charge equations of a simpler type than those holding in the main part of the cathode dark space can be applied to it, and that the results obtained in this way are, on the whole, consistent with those obtained by other means.

4. *Summary.*

The primary dark space on the cold cathode of a Geissler discharge is similar in appearance to the positive ion sheaths present on negative exploring electrodes. A number of its properties can be accounted for by application of the equations developed by Langmuir for the latter, but there are discrep-

ances between the observed and calculated current densities which indicate that the cathode is receiving fast electrons from adjacent parts of the discharge, which, in turn, could produce a secondary emission of electrons from the metal. The primary dark space may be the analogue in a glow discharge of the cathode sheath in an arc.

References.

(1) F. W. Aston, Roy. Soc. Proc. lxxx. p. 45 (1908).
(2) Aston and Watson, Roy. Soc. Proc. lxxxvi. p. 168 (1912).
(3) Kossel. *Jahrb. d. Radioakt.* xviii. p. 326 (1921).
(4) Holst and Oosterhuis, *Physica*, i. p. 78 (1921).
(5) Penning, *Zeit. f. Physik*, xl. p. 4 (1926).
(6) K. T. Compton and Morse, Phys. Rev. xxx. p. 305 (1927).
(7) Güntherschulze, *Zeit. f. Phys.* xxxiii. p. 810 (1925).
(8) Güntherschulze, *Zeit. f. Phys.* xxxvii. p. 868 (1926).
(9) Brose, *Ann. d. Phys.* lviii. p. 731 (1919).
(10) Seeliger and Lindow, *Phys. Zeit.* xxvi. p. 393 (1925).
(11) Langmuir, Journ. Franklin Inst. cxcvi. p. 751 (1923).
(12) J. J. Thomson, Phil. Mag. iv. p. 1128 (1927).
(13) Ryde, Phil. Mag. xlv. p. 1149 (1923).
(14) Langmuir and Mott-Smith, Gen. Elect. Rev. xxvii. p. 554 (1924).
(15) Emeléus and Harris, Phil. Mag. iv. p. 49 (1927).
(16) Aston, Roy. Soc. Proc. civ. p. 565 (1923).
(17) Güntherschulze, *Zeit. f. Phys.* xx. p. 1 (1923).
(18) Güntherschulze, *Zeit. f. Phys.* xxxiv. p. 549 (1925).
(19) Jackson, Phys. Rev. xxx. p. 473 (1927).
(20) Emeléus and Carmichael, 'Nature,' Jan. 7, 1928.
(21) See Bär, *Handb. d. Physik*, (Geiger-Scheele), xiv. p. 190.
(22) Clarkson, Phil. Mag. iv. p. 849 (1927).
(23) Compton, Turner, and McCurdy, Phys. Rev. xxiv. p. 597 (1924).
(24) K. T. Compton, Phys. Rev. xxi. p. 266 (1923).
(25) Slepian, Phys. Rev. xxvii. p. 407 (1926).

CVI. *Magnetism and the Structure of some Simple and Complex Molecules.* *By* D. M. Bose, *Ghosh Professor of Physics, Calcutta University* *.

IN the present paper it is proposed to discuss some recent theories on the structure of some simple and complex molecules in light of their magnetic properties. Before we can proceed further with our discussion, it will be necessary to give a short account of these theories.

Structure of diatomic molecules.

The nature of the bond between the atoms of a diatomic molecule can be of two kinds, viz.: polar and non-polar or

* Communicated by the Author.

contravalent and covalent. In the former by the transference of one or more electrons from one atom to the other, each is left with an outer configuration of eight electrons, with an excess of deficiency of negative charge. The two ions so formed are held together by electrostatic forces, and can be ionized in solution. In the case of the union of two atoms of the same type and other non-ionizable molecules, the nature of the forces holding the two atoms of the molecule is obscure, but it is assumed that two atoms, each of which is a few electrons short of a stable number, can share electrons in such a way that each of the latter is considered to be constituent of both the atoms, and thus form links which are not entirely due to electrostatic attractions and so cannot be ionized. Lewis showed that in a large class of non-polarizable compounds, the total number of electrons in the outer shells of the atoms taking part in them is even.

From this the conclusion is drawn that the chemical bond in them is due to pairs of electrons moving in binuclear orbits. Such bonds are known as covalent bonds. Recently a new theory of the distribution of valence electrons in diatomic molecules has been proposed by Mulliken, Birge, and Mecke *, from their study of the band spectra of diatomic molecules.

The total energy of a molecule is made up of the electronic energy of the radiating electrons, the oscillatory energy of the atomic vibrations, and the energy of rotation of the molecule as a whole. We have now a more or less complete theory of the band spectra so far as the rotational and oscillatory energies of the molecule are concerned. In recent years a great deal of attention has been directed to the interpretation of that part of the band spectra which is due to the quantum jumps of the radiating electrons. From the recently acquired insight into the relation between spectral terms and the number and distribution of the emitting electrons in the different quantum orbits in an atom, it has been possible by the analysis of the electron part of the band spectra of molecules, to assign spectral terms to them, and from that to deduce the distribution of the electrons responsible for these terms, in different quantum orbits. Thus it has been found that spectra of diatomic molecules like BeF, BO, CN, show great similarity to that of Na, while CO gives a spectra similar to Mg, and so on. The

* For references see Mecke and Guillery, "Report on Band Spectra," *Phys. Zeit.* xxviii. pp. 479, 514 (1927).

total number of electrons in the first group of diatomic molecules is thirteen, which, according to the hypothesis put forward by Birge and Mulliken, are distributed as follows—each of the nuclei retains its two K-electrons, of the remaining nine outer electrons, eight form an octet shell enclosing the two nuclei, while the ninth electron moves in a 3-quantum orbit, giving rise to a ^2S term.

Thus we can arrange these diatomic molecules, according to the total number of outer electrons found in them, as follows (Table I.) :—

Table I.

Molecules.	Total No. of Outer Electrons.	No. of Electrons outside octet shell.		Expected ground terms.
		$l=0$.	$l=1$.	
BF, BeO, CN	9	1	—	^2S
N_2, CO	10	2	—	^1S
NO	11	2	1	^2P
O_2	12	2	2	^3P, ^1D, ^1S

If the analogy between these diatomic molecules and the corresponding atoms is to be maintained, it has to be shown that these molecules are capable of entering into chemical combination with a valency proportional to the number of electrons which lie outside the common octet shell. It will be seen later in what sense this expectation is realized.

When one of the combining atoms is hydrogen the molecules form non-metallic hydrides, the total number of electrons in their outer shell can be eight or fewer. These hydrides have been termed by Grimm * as pseudo-atoms, with chemical properties similar to the atoms having the same number of electrons in the outer shells, as can be seen from the following Table II.

Band spectra of these hydrides show that round each hydrogen nucleus two electrons move in a closed orbit with zero impulse moment.

* Geiger and Scheel, *Handbuch der Physik*, vol. xxiv. Grimm, 'Atombau u. Chemie,' p. 512.

TABLE II.

Hydrides.	No. of Outer Electrons.	Corresponding Atoms.
OH, NH_2	7	F
FH, OH_2, NH_3	8	Ne
CH_4		

Coordination Compounds.

The second class of molecules with which we have to deal are the so-called coordination compounds of Werner*. A typical example is $Pt(NH_3)_6.Cl_4$. Here the Pt atom is capable of holding, not only the four Cl atoms by its electrovalency, but it can also further combine with six of such apparently stable molecules like NH_3. In solution all the four Cl atoms are found to be ionized, while the six ammonia molecules are found to be attached to the central atom by non-ionizable bonds. The characteristic properties of such complexes have been summarized by Sidgwick as follows:—

(1) Their structures appeared to be quite independent of the rules of valency, according to which the numerical value of the valency of an atom element was primarily determined by the group in the periodic table to which it belonged. In these compounds the structure was determined rather by the tendency of four or six atoms or groups to arrange themselves round a central atom.

(2) In them a univalent atom or group of atoms, such as Cl or NO, could be replaced by apparently saturated molecules like H_2O or NH_3, without affecting the stability of the complex.

(3) Such replacements are always accompanied by a change in the ionization of the molecule. Thus, taking the above complex compound $Pt(NH_3)_6Cl_4$, we find that the NH_3 molecules can be replaced one by one, until $Pt(NH_3)_2Cl_4$ is

* I am indebted for the following account of Werner's theory of coordination compounds and Dr. Sidgwick's explanation of the origin of coordination links to the very interesting and suggestive address delivered by Dr. Sidgwick as President of the Chemistry Section of the B.A. Meeting, held at Leeds in September 1927. See 'The Advancement of Science,' 1927.

reached, which is not ionized at all. Here every molecule of NH_3 in the complex group $Pt(NH_3)_6^{++++}$ is replaced by a Cl atom with a consequent diminution of its positive charge. If, now, more NH_3 are replaced ionization occurs again, but the complex has received a negative charge, and we finally have the double salt K_4PtCl_6.

Werner proposed to explain these phenomena by assuming that round the central atom of the complex there is a tendency for groups of atoms or molecules to attach themselves in definite numbers (usually six, sometimes four or eight). These groups occupy the first coordination sphere of combination of the central atom, and together with the latter form a coordination complex ; the complex molecule might also contain other atoms or groups occupying a second sphere, which are less firmly attached, *e. g.*, in the above-mentioned compound, the NH_3 molecules are attached to the first sphere of platinum and satisfy the coordination number six, while the four Cl atoms are attached to the second sphere. Experimentally the groups attached to the second sphere were distinguishable by the fact that they were ionized by water, while those forming part of the coordination complex were not. Recent X-ray analysis of the crystalline structures of some of these coordination compounds of platinum have confirmed Werner's theory of their structure *.

Werner himself has not given any picture of the nature of the forces which held the groups of atoms to the first coordination sphere. Kossel, who had successfully explained the formation of polar compounds by electrical forces, tried to apply the same ideas to explain the formation of complex molecules. But his views have not been generally accepted and we will not therefore go into the details of his theory.

Recently Sidgwick † has given a new interpretation of the nature of the bonds which hold atoms or atomic groups to the first coordination sphere of the central atom. According to modern electrical theories only two kinds of bonds are possible, viz., electrovalent and the covalent, the one due to the transference and the other due to the sharing of electrons between two atoms—the former is ionizable, the latter is not. Sidgwick supposes that the coordination bonds being non-ionizable belong to the latter type. But they must arise in a way different from the ordinary covalent bonds, since their number is not related to the periodic group of the central atom, and they can combine with atoms

* See Wycoff, 'The Structure of Crystals.'

† *Loc. cit.*

(like N in NH_3 or O in OH_2) which have already completed a stable number of electrons. In the normal covalency it is assumed that each of the two atoms contributed an electron to the link. Sidgwick extends the idea by supposing that both the electrons may be provided by one of the atoms. According to him the conditions for the formation of a coordination link are that we should have : (i.) one atom which has a pair of valency electrons to offer ; and (ii.) another which has room for one or more pair of electrons in its valency group. He calls the former atom which lend a pair of electrons the donor and the latter atom the acceptor. As an example of such formation he considers the combination of NH_3 with BCl_3. In the former the N atom, which has five electrons in its valency group, of which three are shared with the three H atoms, leaving a pair of electrons to share, is the donor; in the latter the B atom which has all its valency electrons shared with the three Cl atoms, and has two vacant places in its valency group, is the acceptor. Their combination is represented as follows :

$$\begin{array}{ccc} \text{Cl} & \text{H} & \text{Cl}\ \text{H} \\ \text{Cl}:\underset{\text{Cl}}{\overset{\cdot\cdot}{\text{B}}} + :\underset{\text{H}}{\overset{\cdot\cdot}{\text{N}}}:\text{H} & = & \text{Cl}:\underset{\text{Cl}}{\overset{\cdot\cdot}{\text{B}}}:\underset{\text{H}}{\overset{\cdot\cdot}{\text{N}}}:\text{H} \end{array}$$

In this compound the atoms B and N assume a maximum covalency or coordination number of four, and round each an octet valency shell is completed.

Sidgwick extends this reasoning to the case of a regular coordination compound like $[Cr(NH_3)_6]Cl_3$. Here the Cr atom stripped of its three valency electrons forms the ion Cr^{+++} with a stable core of 21 electrons (of which three are in the M_3 shell). It has no valency group left and the core is stable, as proved by the stability of the chromic salts. This ion can form a series of coordination links with NH_3 molecules, by sharing the lone pair of electrons of the N atom. It is assumed that in the case of these types of compounds the stable size of the valency group is 12, as opposed to 8 in the previous case considered, and therefore 6 molecules of NH_3 will be taken up. In case of one of the NH_3 molecules being removed from the first coordination sphere, it takes away with it the two shared electrons which it contributed ; the Cl atom which replaces it moves from the second to the first coordination sphere. It can only supply one electron to the link, the other has to be supplied by the central atom. Thus the electrovalency of the latter is reduced by one, giving instead of $[Cr(NH_3)_6]^{+++}$, the ion

$[Cr(NH_3)_5Cl]^{++}$, or the salt $[Cr(NH_3)_5]Cl_2$. The same change will occur for every replacement of a whole molecule in the complex by a univalent radicle. Thus the peculiar change of electrovalency noted by Werner in this class of compounds is explained. The chief assumption in the above theory is of the existence of a stripped atom with a stable core round which *a new valency shell* of 12 electrons can be formed by six stable molecules sharing pairs of electrons with it. In case one of the latter is replaced by a univalent radicle, one of the shared electrons is supplied by the central atom.

Besides Cr^{+++} other ions of elements belonging to the first transition group like $Fe^{++}Fe^{+++}Co^{+++}Ni^{++}$, etc., form stable coordination compounds. In all of them the M_3 shell is incomplete, and the interesting question arises whether the 12 electrons which, according to Sidgwick, form a new valency group, lie entirely outside this M_3 shell or some of them occupy vacant places in it. As these ions are paramagnetic and their moments depend upon the number of electrons in their M_3 shell, it will be seen later that some definite information can be obtained by considering the magnetic moments of this class of coordination compounds. Further, in this class of compounds some of the groups of atoms or molecules which enter into co-ordination bond with the central atom are the following: Cl, OH, OH_2, NH_3, CN, CO, NO, O_2, and N_2H_4—they represent types of molecules whose structures we have discussed in the first portion of this paper, in light of evidence obtained from band spectra. It will be seen from evidence presented later that Cl, OH, and CN contribute only one electron to a coordination link, OH_2, NH_3, and O_2 contribute two, NO contributes one or three, and N_2H_4 contributes four. We shall see later what relation there exists between the numbers of electrons contributed by these molecules, and their structures which have been suggested by the theories of Mulliken and Birge.

We will now proceed to test the above theories of Mulliken and Birge on the structure of diatomic molecules, and of Sidgwick on the nature of coordination links, by considering the magnetic properties of coordination compounds in which the central atom belongs to the first transition group of elements. It will be necessary here to interpose a short account of a theory of paramagnetism recently proposed by the writer *, to account for the behaviour of atoms and ions of this group of elements.

* *Zeit. f. Phys.* xliii. p. 864 (1927).

Hund* has given a method of calculating the magnetic moments of atoms and ions from a knowledge of the number of electrons contained in any incomplete shell in the latter, and their quantum numbers. Every electron moving in a closed orbit is characterized by four quantum numbers, n, l, m_l, and m_s. For electrons belonging to the same shell, the values of n and l are the same, while the m_l and m_s are different. Here $-l \leqq m_l \leqq l$ represents the orbital moment of an electron, and $-\frac{1}{2} \leqq m_s \leqq \frac{1}{2}$ represents its spin moment. If there are z electrons in any incomplete shell, we have to take the sum of the orbital and spin moments separately, and thus get two numbers $\bar{s} = \sum_z m_s$ and $\bar{l} = \sum_z m_l$. The inner quantum number j is the vectorial sum of these two resultants, where $|l - \bar{s}| \leqq j \leqq \bar{l} + \bar{s}$. The largest number of electrons which can occupy any shell is $2(2l+1)$, and when $z \leqq 2l+1$, the value of j corresponding to the ground term is equal to $|\bar{l} - \bar{s}|$, and for $z \geqq 2l+1$ the corresponding value of j is $\bar{l} + \bar{s}$.

The magnetic moment μ of an ion with z electrons is given by $\mu = jg$, where

$$g = 1 + \tfrac{1}{2} \frac{j(j+1) + \bar{s}(\bar{s}+1) - \bar{l}(\bar{l}+1)}{j(j+1)}$$

is Lande's anomalous Zeeman effect factor. On going through the calculation it is found that if the magnetic moment of the ion is expressed in terms of Weiss's magnetons n_W, then

$$n_W = 4{\cdot}97 g \sqrt{j(j+1)}. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

As has been shown in my paper†, that though Hund's formula gives a very good representation of the magnetic moments of the tri- and tetra-valent ions of the rare earth groups of elements, it fails entirely to account for the ions of the iron group. It has been shown there that a much better agreement with the experimentally determined values can be obtained, if in Hund's formula we put $\bar{l} = 0$, which interpreted physically means that only the spin moments of the electrons contribute to the magnetic moment of the ion. On making this substitution we get $j = s$ and $g = 2$. The value of n_W now comes out to be

* *Loc. cit.* xxxiii. p. 361 (1925).
† *Loc. cit.*

$$^{*}n_{W}=4{\cdot}97\sqrt{z(z+2)} \text{ for } z\leqq 2l+1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\text{and} \quad =4{\cdot}97\sqrt{z'(z'+2)} \text{ for } z\geqq 2l+1 \text{ where } z'=2(2l+1)-z. \quad . \quad . \quad . \quad (3)$$

The physical interpretation of the last formula is as follows: the maximum number of electrons which can occupy a shell with the azimuthal quantum number 1 is $2(2l+1)$. Of these the first $2l+1$ electrons are free to align themselves in an external magnetic field. When the number of electrons z exceeds this value, then only $z'=2(2l+1)-z$ of them are free to align themselves, while the rest equal to $z-z'=2(z-\overline{l+1})$, mutually neutralize one another in pairs and therefore are not influenced by any external field.

TABLE III.

z.	$n_{W\,(calc.}$	$n_{W\,(obs.)}$	
		Simple salt.	4-fold coord. comp.
1.....	8·6	V^{IV} 8–9 [1]	
2.....	14·1	V^{+++} 12·6 [2]	
3.....	19·2	Cr^{+++} 18·3	
4.....	24·4	Cr^{++} 24 Mn^{+++} 25	
5.....	29·4	Mn^{++} 29 Fe^{+++} 29	
6.....	24·4	Fe^{++} 26–27	24·1
7.....	19·2	Co^{++} 25	21·3
8.....	14·1	Ni^{++} 16–17	14·8
9.....	8·6	Cu^{++} 9·1	

[1] Perrakis, *Compt. Rend.* clxxxv. p. 110 (1927).
[2] Bose and Bhar, to be published shortly.

In Table III. are given the calculated and experimentally determined values of n_w corresponding to the different number of electrons z in the M_3 shell of the ions belonging

* If the magnetic moments are expressed in terms of Bohr's magnetons μ_B, then

$$n_B=z \text{ for } z\leqq 2l+1$$
$$=2(2l+1)-z \text{ for } z\leqq =2l+1.$$

to the elements of the first transition group. The theoretically calculated values of n_W are obtained by means of equations (2 & 3) proposed by me. The experimentally determined values are mostly taken from Stoner's book. In the last column are given the values of n_W for the fourfold coordination compounds of these elements, and are taken from some recent measurements made by Messrs. P. Ray and H. G. Bhar. On looking through the table it will be found that there is fairly satisfactory agreement between the calculated and experimentally determined values of n_W for ions in which the number of electrons z in the M_3 shell is less than or equal to $2l+1$, viz. (5). But for values of z greater than this, there is serious discrepancy between the two sets of values; there is considerably better agreement, however, between the calculated values of and those found for the fourfold coordination compounds of these ions.

In Table IV. I have given the number of magnetons contained in certain fourfold compounds of Fe, Co, Ni, and Cu, and compared them with the values to be theoretically expected from the number of electrons in the M_3 shell of the central atom of the complex.

TABLE IV.

Compounds.	$n_{w\,(obs.)}$	$n_{w\,(calc.)}$
$[Fe(N_2H_4)_2]Cl_2$	24·1	24·4
$[Co(N_2H_4)_2]SO_3, H_2O$	21·3	
$[Co(N_2H_4)_2](CH_3COO)_2$	22·6	
$[Co(N_2H_4)_2]Cl_2$	24·4	19·1
$[Co(C_2H_5N)_4](SCN)_2$	24·0	
$[Ni(N_2H_4)_2]SO_3$	14·96	
$[Ni(N_2H_4)_2](NO_2)_2$	14·76	14·1
$[Ni(NH_3)_4]SO_4$ [1]	13·00	
$[Cu(NH_3)_4](NO_3)_2$ [1]	9·00	8·6

[1] Rosenbohm *loc. cit.*

All these compounds with the exception of the last two have been prepared in the Science College by Messrs. P. Ray and H. G. Bhar, with whose permission their results are given here. It has been found that the Hydrazine compounds give values for the magnetic moments which approach most

closely the theoretically expected values. That the agreement is not always good is evident from the table. In these fourfold compounds, each N_2H_4 group is assumed to contribute two pairs of coordination links to the central atom. Due to the presence of these four coordination links the magnetic moments of the central ion remain either unaltered or are brought up to values which we should expect when the spin moments of the electrons on the M_3 shell are alone effective. I have taken this as a magnetic test of a satisfactory coordination linkage, viz., when the magnetic moment of the complex compound—corrected for diamagnetism—approaches very nearly the value to be expected from the number of electrons on the M_3 shell of the central atom. We conclude therefore that in a fourfold coordination compound the central atom, stripped of its valency electrons, is attached to the atomic groups forming the complex by four pairs of coordination electrons. These electrons form an octet shell which lies outside the M_3 shell of the central atom. The structure of these compounds is similar to that of the CH_4 molecule.

Sixfold Coordination Compound.

We proceed next to consider the six-fold coordination compounds—which differ from the fourfold compounds in having two extra pairs of coordination bonds of four electrons. We shall show that these four extra electrons can under circumstances occupy, either the vacant places in the M_3 shell of the central atom, or orbits which lie quite outside the latter.

In Table V. are given a number of sixfold compounds of Cr, Fe, Co, and Ni. In columns 2 and 3 are given the principal valency of the central atom and the corresponding

TABLE V.

Complex compound.	Simple ion.	z_1.	$n_{w\,(obs.)}$	$n_{B\,(calc.)}$	z_2.
$[Cr^{+++}(NH_3)_6](NO_3)_2$	Cr^{+++}	3	20·0	3(19·2)	7
$K_4[Fe^{++}(CN)_6]$	Fe^{++}	6	dia.	0	10
$K_3[Fe^{+++}(CN)_6]$	Fe^{+++}	5	10	1(8·6)	9
$[Co^{+++}(NH_3)_6]Cl_3$	Co^{+++}	6	dia.	0	10
$[Ni^{++}(N_2H_4)_3]Cl_2$	Ni^{++}	8	13·97	2(14·1)	8+4
$[Ni^{++}(N_2H_4)_3]SO_3, H_2O$	Ni^{++}	8	13·6	2(14·1)	8+4

number of z_1 of electrons in their M_3 shells. In column 4 the experimentally determined number of Weiss' magnetons contained in these compounds are given, the corresponding number of Bohr's magnetons n_B are to be found in column 5. Knowing the value of n_B the number of electrons actually present in the M_3 shell of the central atom is calculated according to the formula

$$n_B = z' = 2(2l+1) - z_2 = 10 - z_2, \quad . \quad . \quad . \quad (3)$$

their values are given in column 6. From the above we see that in every sixfold compound, with the exception of those of nickel, the number of electrons in the M_3 shell of the coordinating atom is greater by four than that in the corresponding simple ion. Ni^{++} has already 8 electrons in its M_3 shell and there is no room for four extra electrons which we assume to move in orbits lying entirely outside the M_3 shell. This keeps the magnetic moment of the nickel salt unaltered by the addition of six coordination bonds. Another such example of a cobalt compound is given in Table VI. We therefore conclude that in a sixfold compound, four pairs of the electron links form an octet shell whose orbits lie entirely outside the M_3 shell of the central atom; the four electrons of the remaining two links may occupy the M_3 shell or not, according as there is room for all of them there or not. The results we have obtained confirm on the whole Sidgwick's theory of the formation of a fresh valency group by the coordination electrons, but give a more detailed picture of how they are distributed, viz., eight of them form an octet shell round the central ion and the remaining four try to fit themselves in the M_3 shell of the latter, if there is room for all of them; otherwise they move in orbits outside the M_3 shell and their resultant magnetic moment is null.

Structure of Diatomic Molecules.

We now turn to the second part of our investigation, which is to find out what information we can get from a study of these coordination compounds, of the structure of diatomic and similar molecules.

A number of coordination compounds, in which the atomic groups NH_3, N_2H_4, OH, OH_2, CN, CO, and O_2 are attached to the primary coordination spheres, are given in Table VI. In column 2 are given the number of Bohr's magnetons contained in them. In column 3 are given the atomic groups whose contribution of coordination electron

are placed in the last column. Every one of the coordination compounds satisfies our magnetic test, viz., they have magnetic moments which are very nearly multiples of Bohr's magnetons. Wherever possible only such compounds are

Table VI.

Coordination Comp.	n_B.	Atomic group.	Contribution to coordination.
$[Co(NH_3)_6]Cl_3$[1]	0	NH_3	2
$[Co(NH_3)_5Cl]Cl_2$[1]	0	Cl	1
$[Co(NH_3)_5(NO)]Cl_2$[2]	0	NO	1
$[Co(NH_3)_5(NO)](NO_3)_2$[2]	2	NO	3
$[Co(NH_3)_4(OH)(OH_2)]SO_4$[1]	0	OH_2	2
$[Co(NH_3)_5(OH)](NO_3)_2$[1]	0	OH	1
$\begin{pmatrix} Co(NH_3)_5 \\ \vert \\ O_3 \\ \vert \\ Co(NH_3)_5 \end{pmatrix}^3 SO_4$	0	O_2	2
$[Ni(NH_3)_4]Cl_2$[1]	2	NH_3	2
$[Ni(N_2H_4)_2]Cl_2$	2	N_2H_4	4
$Fe(CO)_5$[4]	0	CO	2
$[Fe(CN)_6]K_4$[5]	0	CN	1
$[Fe(CN)_5(NO)]Na_2$[3]	0	NO	3

[1] Rosenbohm, *Zeit. f. phys. Chem.* xciii. p. 693 (1919).
[2] P. Ray & H. Bhar to be published shortly.
[3] Feytis, *C. R.* clii. p. 708 (1911).
[4] Oxeley, Proc. Camb. Phil. Soc. xvi. p. 102 (1911).
[5] Welo, 'Nature,' cxvi. p. 359 (1925).

selected for which $n_B = 0$, *i. e.* they are diamagnetic. From the value of n_B it is at once possible to find out what is the number of electron links supplied by each of the atomic groups.

Starting with a hexamine compound of cobalt, we find that each NH_3 molecule supplies two electrons to the central atom. In the next compound, a NH_3 molecule has been replaced by a Cl atom without altering the magnetic moment of the compound ; the electrovalency of the complex has been reduced by unity, from which we conclude that the Cl atom contributes only one electron to a co-ordination link, the other is supplied by the Co atom. In

the third compound the Cl atom inside the complex has been replaced by a NO molecule without in any way disturbing the complex. We thus conclude that here the NO molecule supplies only one electron to a coordination link. The fourth compound, though exactly similar to the third, contains two Bohr's magnetons. This behaviour can only be explained on the assumption that here the NO molecule supplies three electrons to the coordination links instead of one, as in the previous case. This can be explained as follows :—The central atom Co is divalent in this compound, and therefore contains 7 electrons in its M_3 shell. The five NH_3 molecules associated with it contribute 10 shared electrons and if the NO molecule only contributed one electron there would altogether be $7+10+1=18$ electrons moving in the outer orbits of which 10 would be in the M_3 shell and the other 8 would form into an octet shell. Such a distribution would make the complex diamagnetic, which it is not. On the other hand, if NO contributes three electrons, the total number of outer electrons becomes $7+3+10=20$, which can only be distributed in the following way :— 8 electrons on the M_3 shell, and the remaining 12 electrons in 6 pairs of orbits which lie outside the latter. With such a distribution the magnetic moment of the complex comes out to be $10-s_2=10-8=2$, as is found experimentally. This conclusion is supported by considering the nitroso-compound of iron which is placed last in the table. To make a compound like $K_4[Fe(CN)_6]$ diamagnetic, it is necessary to assume that each CN group contributes one electron each to a coordination link, the other six are made up by the central atom contributing two, and the four K atoms contributing one each. On replacing a CN by a NO group inside the complex, it is found that the magnetic moment of the latter remains unchanged, while its electrovalency is reduced by two, which can only be accounted for by supposing that the NO molecule contributes three electrons to the coordination links. Thus we see that a NO molecule can contribute either one or three electrons to coordination links. The contributions to coordinate links made by the remaining atomic groups like OH, OH_2, CO, O_2, and N_2H_4, can be inferred without difficulty from the table.

The relation between the structure of these molecules and the number of coordination links they contribute is summarized in Table VII. In column 2 the total number of electrons in the outer shells of the combining atoms are shown distributed amongst the different quantum levels according to the structure of such molecules proposed by

Mulliken and Birge. In column 3 are given the distribution of the actual number of electrons which are available for the formation of coordination links; we obtain this number by subtracting from the number of electrons in the

TABLE VII.

Atomic groups.	No. of electrons in outer orbits.		No. of electrons available for sharing.				Actual contributions to coord. links.
			$n=2$.		$n=3$.		
	$n=2$.	$n=3$.	$l=0$.	$l=1$.	$l=0$.	$l=1$.	
Cl	7	—	2	5			1
OH	7	—	2	3			1
NH_2	7	—	2	1			
N_2H_4	7+7	—	2+2	—			4
OH_2	8	—	2	2			2
NH_3	8	—	2	0			2
CN	8	1			1	—	1
CO	8	2			2	—	2
NO	8	3			2	1	3, 1
O_2	8	4			2	2	2

valency shell of the molecule, those which have already taken part in a covalent bond, *e. g.*, in the case of NH_3, the 3H atoms form covalent bonds with three of the five outer N electrons, so that only two of the latter are available for coordination links.

In the last column the actual contributions made by these atomic groups are given. Leaving for the present the N_2H_4 group, we can divide the other atomic groups into the following classes :—(i.) Those in which the total number of outer electrons is less than 8, with them the tendency is to form covalent bonds with the central atom, so as to complete their own octet configurations ; (ii.) those in which the outer electrons form an octet, but some of the electrons have entered into covalent bonds, they contribute a pair of electrons to the central atom, all of which come either from the shell $l=1$ or $l=0$; (iii.) those in which the number of outer electrons exceed eight ; the surplus electrons are

assumed to move in three quantum orbits with $l=0$ and $l=1$. Some or all of these electrons can take part in co-ordination links, so as to leave the number of unshared electrons in the shell $l=0$ either two or zero.

We infer that besides the octet shell, the two electrons in the shell $l=0$ form a stable configuration similar to what occurs in atomic distributions. There is, however, this difference that the valency electrons of such molecules are not detachable, and they cannot therefore give rise to polar bonds. Coming back to the consideration of the atomic group N_2H_4, it can be regarded as due to the combination of two NH_2 groups. The structure of the latter can be represented graphically as follows $:\dot{\underset{\cdot\cdot}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{H}}}}}}\mathrm{N}\cdot$, a combination of two such groups will give rise to a new one

$$:\dot{\underset{\cdot\cdot}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{H}}}}}}\mathrm{N}\cdot + :\dot{\underset{\cdot\cdot}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{H}}}}}}\mathrm{N}\cdot = :\underset{\cdot\cdot}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{H}}}}}\mathrm{N}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{H}}}}}:$$

in which each of the N atoms has eight electrons in its valency shell of which six take part in covalent links. There are therefore $2+2=4$ electrons in the N_2H_4 molecule available for taking part in coordination links, and this is the actual number of electrons they supply to a coordinating atom.

We thus find that the model of diatomic and similar non-polar molecules inferred from the study of Band Spectra can satisfactorily account for the number of coordination links which these atomic groups can supply.

In this connexion it will not be out of place to consider the criticism of the Birge-Mulliken structure of diatomic molecules which has recently been made by Stoner in an interesting paper * entitled "Magnetism and the Structure of Molecules." The principal point in Stoner's criticism is the failure of these models to account for the experimentally determined values of the magnetic moments of NO and O_2. The following Table VIII., taken from his paper, gives a comparison between the calculated and experimentally determined values of n_W for these molecules based on Hund's theory. In the last line I have given the values to be

* Phil. Mag. iii. p. 351 (1927).

expected on the modification of Hund's theory which has been put forward by me.

TABLE VIII.

Molecule.		NO.		O_2.				
n_w (obs.)		9·20		14·12				
Theoretical ground terms.		^2P		^3P			^1D	^1S
		$^2P_1$	$^2P_2$	$^3P_0$	$^3P_1$	$^3P_2$	$^1D_2$	$^1S_0$
n_w (calc.)	Hund	2·9	13·8	0	10·6	18·2	12·2	0
	Bose	8·6		14·2				

The assumption that only the spin moment of the electrons in the outer valency shell of these molecules leads to values for their magnetic moments which are in excellent agreement with the experimental values. This furnishes another proof of the validity of this assumption.

Discussion.

It will be useful here to sum up the results we have obtained up till now. We started with the assumption that the paramagnetic moments of the compounds of the elements belonging to the first transition group are due only to the spin moments of the electrons present in their incomplete shells. On comparing the values of the magnetic moments calculated according to this assumption with those found experimentally, it was found that up to manganese the agreement was satisfactory, but the simple salts of the ferromagnetic elements gave values of magnetic moments considerably larger than the expected ones. This deviation seems to be associated with the addition of the sixth, seventh, and the eighth electrons to the M_3 shell of these atoms, where, according to Pauli's equivalence theorem, they begin to form neutral doublets with an equal number of electrons out of the first five already present on the shell. If it is supposed that the alignments of the newly added electrons to form neutral doublets is not perfect, then the deviations

noted can be accounted for. This surmise is strengthened by the discovery that certain fourfold coordination compounds of these elements have magnetic moments which are in good agreement with the theoretical values. According to the conception of Sidgwick, in a fourfold coordination compound, a new octet shell of valency electrons is formed round the core of the central atom, and this helps to stabilize the electron orbits on the outer core of the central atom. We are not in a position to say why all the fourfold coordination compounds of, say, cobalt, have not the theoretically expected magnetic moments. Further investigations on this point are being carried out.

In the case of the sixfold coordination compounds, according to Sidgwick, the size of the valency shell formed round the core of the central atom was increased to accommodate twelve instead of eight electrons. Magnetic evidence, however, points to the interpretation, that where there is room for all the four extra electrons in the M_3 shell of the central atom, the octet shell is not disturbed but the extra electrons are accommodated in the M_3 shell. Where there is no accommodation for all of the four in the M_3 shell, these four move in orbits outside the latter. It is found, however, that in the latter case the compounds are not very stable.

In connexion with the coordination compounds, two further questions arise to which no satisfactory answer can be given at present. The first is what limits the number of coordination groups that can be associated with a central atom? Sidgwick seems to think with Main Smith that it is the quantum number of the outer electrons of an element is the determining factor, *e. g.*, the maximum covalency of hydrogen is 2, of the elements of the first period (Li to F) is 4, of the elements of the second short period (Na to Cl) and of the first long period (K to Br) is 6, and of the later elements is 8.

The other view is of Kossel who supposes that the number depends on the atomic volume and the charge on the central ion—these two determine the number of molecules which can cluster round the central atom.

This brings us to the second question, viz., whenever a definite number of molecules cluster round the central core, is there a sharing of electrons between the latter and each of the former? It can be shown that in certain cases no such coordination links exist, *e. g.*, the compound $FeSO_4$, $7H_2O$, has exactly the same magnetic moment as the anhydrous salt $FeSO_4$. The former, which can be written as $[Fe(H_2O)_6]SO_4, H_2O$, was considered by Werner to be a

true coordination compound, and as such it ought to have been diamagnetic; $[Ni(NH_3)_6]Br_2$ has been found by Rosenbohm to have 16 Weiss's magnetons, the same as that contained in the simple salts. According to our theory the magneton number ought to have been about 14, as is the case with a similar compound $[Ni(N_2H_4)_3]Cl_2$. Here it seems doubtful whether the NH_3 molecules are in coordination link with the central atom. We can think of other kinds of forces which can hold the NH_3 molecules to the central atom, viz., the latter stripped of its valency electrons is left with a positive charge. Molecules with large dipole moments like H_2O, NH_3 can be attracted to form clusters round such a charged ion, and the maximum number that can be attached depends upon the atomic volume of the latter. Blitz* has calculated the heat of reaction which is given out by the addition of a varying number of NH_3 molecules in the space lattice of a simple salt. The original salt lattice is expanded to accommodate $n$$NH_3$ molecules, and suppose E is the work done. If A′ is the energy set free by the association of n molecules of NH_3 round each salt molecule, then $\phi_n = A' - E$, where ϕ_n is the heat of reaction due to this process. It is found, for example, that the value of $\frac{A'}{n}$ for the association of NH_3 molecules to a simple alkali-halogen compound with univalent cation and 8 outer electrons is 14 calories per gm. mol.; when the cation has a double charge it is 28 calories. On the other hand, for the small Li^+ ion with two outer electrons, the value is 21 calories. These numbers give an approximate idea of the forces between dipole molecules and charged ions. It may be that forces of this type attract the atomic groups to cluster round the core of the coordinating atom, and later on, in certain cases, a further linkage is introduced by the sharing of electrons between the atomic groups and the core.

Summary.

1. In this paper the recent theories of the structure of diatomic molecules proposed by Birge and Mulliken, and of the nature of coordination links in Werner's coordination compounds, proposed by Sidgwick, have been tested by the investigation of the magnetic properties of the coordination compounds of the elements belonging to the first transition group.

* Blitz, *Zeit. f. anorg. Chemie*, vol. cxxx. p. 93 (1923).

2. Sidgwick has proposed to account for the linkage of the six atomic groups to the central atom in a sixfold compound by supposing that in general each of the atomic groups contributes two electron orbits to the latter ; all of them taken together form a valency group of twelve electrons round the core of the central atom, which has been stripped of its own valency electrons. From magnetic evidences it is concluded that if there are vacancies in the M_3 shell of the central atom for four electrons, then four out of the twelve shared electrons occupy the M_3 shell, while the remaining eight form an octet shell round the core. When the M_3 shell of the core cannot accommodate all of the four electrons, they move in orbits outside the latter. In the case of fourfold compounds the valency shell of eight electrons contributed by the four atomic groups form an octet shell outside the core of the central atom.

The atomic groups which are usually found in coordination compounds include, amongst others, the following : OH, OH_2, NH_3, CN, CO, NO, O_2, and N_2H_4. Birge and Mulliken have, from Band Spectra evidence, given a new theory of the structure of diatomic non-polar molecules like those included in the above group. It is shown that the number of coordination bonds contributed by these groups can be satisfactorily accounted for on their structures proposed by the new theory.

London,
February 1928.

CVII. *On the Positions of X-Ray Spectra as formed by a Diffraction Grating.* *By* Alfred W. Porter, *D.Sc., F.R.S., F.Inst.P., Professor of Physics in the University of London* *.

IN the calculation of the positions of X-ray spectra as formed by a diffraction grating, it is customary to consider them as Fraunhofer spectra, such as are obtained with gratings in ordinary spectroscopy. In such cases the incident light is a parallel bundle, and so also is the diffracted bundle which is afterwards brought to a point (or line) by a lens. But when X-rays are used, there is no means of producing this parallelism ; the incident beam is always divergent, and the diffracted beam that reaches any one

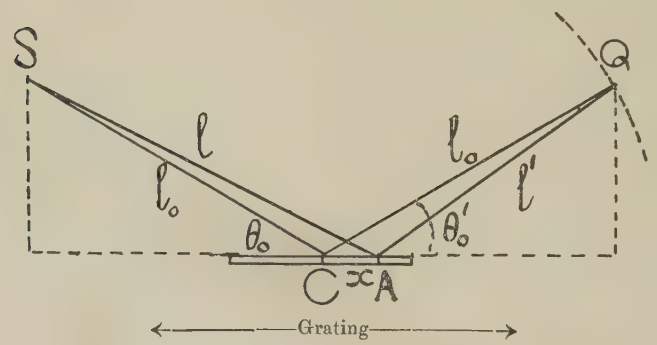
* Communicated by the Author.

point is convergent. For ordinary measurements this is of small importance; but when we consider the extreme accuracy with which X-ray spectral measurements are now being made, the question arises as to what will be the consequence of the lack of parallelism.

The object of this paper is to find a first approximation to the correction which the usual formula needs.

Let S be the source and Q the point on the screen on which the spectra will be formed. For simplicity (and to fit in with common practice) let SC=CQ, where C is the central point of the grating. The ray SAQ is a neighbouring ray reaching the same point. The phases of the effects

Fig. 1.



at Q can be obtained by calculating the sum of the lengths SA=l and AQ=l'. Putting CA=x, we have

$$l = \sqrt{l_0^2 + x^2 + 2l_0 x \cos\theta_0}$$

and

$$l' = \sqrt{l_0^2 + x^2 - 2l_0 x \cos\theta_0'}.$$

The sum $l+l'$ can be written approximately equal to

$$a_0 + b_0 x + c_0 x^2 + g_0 x^3,$$

where

$$a_0 = 2l_0,$$

$$b_0 = \cos\theta_0 - \cos\theta_0',$$

$$c_0 = \frac{1}{2l_0}(\sin^2\theta_0 + \sin^2\theta_0'),$$

and

$$g_0 = -\frac{b_0}{2l_0^2}[1 - \cos^2\theta_0 - \cos\theta_0\cos\theta_0' - \cos^2\theta_0'].$$

The range of retardations for the complete grating of length X is

$$X(\cos\theta_0-\cos\theta_0')$$
$$\left[1-\frac{X^2}{8l_0^2}(1-\cos^2\theta_0-\cos\theta_0\cos\theta_0'-\cos^2\theta_0')\right];$$

the range of phases is obtained by multiplying this by $2\pi/\lambda$; the corresponding coefficients we will represent by a, b, c, and g.

Now in the Fraunhofer case the maximum of order P occurs when

$$\frac{2\pi}{\lambda}(\cos\theta_0-\cos\theta_0')=PN\,.\,2\pi,$$

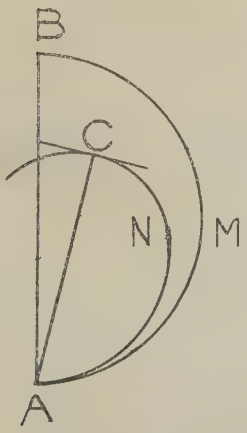
where N is the total number of "lines" on the grating; or, if r is the grating-interval, when

$$r(\cos\theta_0-\cos\theta_0')=P\lambda.$$

We can get some idea of the correction required by calculating also the factor in brackets. If the incidence is nearly grazing, we can write each of the cosines *in the small* term equal to unity, and consequently the range of phases becomes

$$X(\cos\theta_0-\cos\theta_0')\left[1+\frac{X^2}{4l_0^2}\right].$$

Fig. 2.



If we could still take a range of phases $2\pi NP$ as determining a maximum, the correcting factor to the wave-length as usually calculated would be $1+\frac{X^2}{4l_0^2}$.

Although this must give the right order, it is in excess of the true value. Reference to a vibration diagram, in which AMB is the curve for the Fraunhofer case, with its maximum at B, shows that when the curve, such as ANC, is of increasing curvature from A to C, the maximum chord does not correspond to a phase difference of π, but is at a point C such that the tangent thereat is at right angles to the radius vector AC.

We will now obtain a more accurate value.

Taking the middle point C of the grating as origin, the two halves of the grating lie symmetrically on the two sides if the centre of one opening coincides with C. With the exception of this one opening (which need not concern us when the number n on each side is large), the openings can be divided into pairs, so that the vibration due to the κth pair is

$$\begin{aligned}&\cos(pt+a+\kappa br+\kappa^2cr^2+\kappa^3gr^3)\\&\quad+\cos(pt+a-\kappa br+\kappa^2cr^2-\kappa^3gr^3)\\&\quad=2\cos(\kappa br+\kappa^3gr^3)\cos(pt+a+k^2cr^2).\end{aligned}$$

This is very nearly (because κ^2cr^2 is very small compared with a) a simple vibration of amplitude

$$2\cos(\kappa br+\kappa^3gr^3),$$

or approximately

$$2\cos\kappa br_1-2\kappa^3gr^3\sin\kappa br_1.$$

Summing for all the n pairs, the intensity is

$$4\left[\sum_{\kappa=1}^{\kappa=n}\cos\kappa br-\sum_{\kappa=1}^{\kappa=n}\kappa^3gr^3\sin\kappa br\right]^2.$$

The maximum occurs when the differential coefficient of this with regard to br is zero, or

$$\Sigma\kappa\sin\kappa br+gr^3\Sigma\kappa^4\cos\kappa br=0.$$

We are only concerned with the value of br in the immediate neighbourhood of a principal maximum for which $br=2\pi\mathrm{P}$, where P is the order of the maximum. Put, therefore,

$$br=2\pi\mathrm{P}+\alpha;$$

then the condition becomes

$$\Sigma\kappa\sin\kappa\alpha+gr^3\Sigma\kappa^4\cos\kappa\alpha=0,$$

or, because α is small,

$$\Sigma\kappa^3\alpha+gr^3\Sigma\kappa^4=0,$$

i. e.,

$$\frac{n(n+1)(2n+1)}{6}\alpha + gr^3\frac{n(n+1)(2n+1)(3n^2+3n-1)}{30} = 0;$$

or, when n is large,

$$\alpha = -\frac{3gr^3}{5}n^2 = -\frac{3}{20}gr^3\mathrm{N}^2,$$

where N is the total number of elements.

Now for nearly grazing incidence

$$g = \frac{b}{l_0^2},$$

and for a maximum

$$br = 2\pi\mathrm{P} - \frac{3}{20}gr^3\mathrm{N}^2$$

$$= 2\pi\mathrm{P} - \frac{3}{20}br\cdot\frac{\mathrm{N}^2r^2}{l_0^2},$$

and we obtain

$$br\left[1+\frac{3}{20}\frac{\mathrm{X}^2}{l_0^2}\right] = 2\pi\mathrm{P}$$

or

$$r[\cos\theta_0 - \cos\theta_0']\left[1+\frac{3}{20}\frac{\mathrm{X}^2}{l_0^2}\right] = \mathrm{P}\lambda.$$

Assuming nearly grazing incidence, the wave-lengths, calculated in the usual way, require therefore to be multiplied by the factor $1+\frac{3}{20}\frac{\mathrm{X}^2}{l_0^2}$ in order that their true values may be obtained. The following table shows the values of this correcting factor in various cases :—

X. \ l_0.	5 cm.	10 cm.	20 cm.
1 mm.	1·00006	1·000015	1·000004
5 mm.	1·0015	1·000375	1·000094
1 cm.	1·006	1·0015	1·000375

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CVIII. *The Electronic Theory of Valency* *.—Part V. *The Molecular Structure of Strong and Weak Electrolytes:* (a) *Complete Ionization.*

By T. Martin Lowry †.

1. *The Theory of Complete Ionization.*

THE theory of complete ionization had its origin in a physico-chemical study of the properties of solutions; but it was very soon adopted by physicists as an explanation of the high symmetry of the crystal-structures revealed by the X-ray analysis of metallic salts, since this could not be accounted for on the traditional theory that the ions of the salt were united into molecules. The new theory has had a large measure of success in both fields of study, since, on the one hand, the conductivity of solutions of ordinary metallic salts has been calculated for the first time by means of a rationally deduced formula, which is valid up to a concentration of perhaps N/100; on the other hand, many of the physical properties of crystals, such as their linear dimensions and angles, heat of formation, elasticity, refractive index, and infra-red absorption, have been calculated successfully on the assumption that the crystals are aggregates of ions of varying degrees of "hardness," which are drawn together by the electrostatic attraction between their opposite charges, but are also repelled from one another with a force varying inversely as (say) the 6th to the 35th power of the distance. On the other hand, the theory of complete ionization fails to cover the behaviour of those weak electrolytes which obey Ostwald's dilution law, just as completely as the latter law failed to cover the behaviour of highly-dissociated metallic salts. Again, although many of the properties of solid ionic aggregates, such as rock salt or calcite, have been predicted successfully from fundamental data, all attempts to predict the dimensions and behaviour of the carbonate ion itself have failed, since this does not behave as a mere aggregate of carbon and oxygen ions. The object of the present paper is therefore to determine the boundaries of the region within which the theory of complete ionization is valid, to find out the factors which make it inoperative in so many cases, and in particular to study the chemical significance of the classification of electrolytes as "strong" and "weak." The applications of similar

* Parts I., II., and III. Phil. Mag. xlv. p. 1105 (1923), xlvi. p. 946 (1913); Part IV. Phil. Mag. xlvii. p. 1021 (1924).

† Communicated by the Faraday Society.

considerations to the study of crystal-structure will form the subject of a subsequent communication.

In both cases the principal argument put forward will be that, although the ions of a salt are generally prevented from neutralising their opposite electric charges by factors which find their simplest expression in the "octet" rule, there are many cases in which this inhibition does not operate, with the result that the ions can be converted into real molecules, as distinguished from mere aggregates of ions, by the neutralisation of their opposite charges with formation of a chemical "bond." These two groups of compounds correspond broadly with the "strong" and "weak" electrolytes; but the two methods of classification cannot be expected to lead to identical results. Thus, on the one hand, a salt which consists entirely of ionic aggregates may be placed under conditions which are so unfavourable to the independent migration of the ions as to bring it within the group of "weak electrolytes"; and, on the other hand, the bond which holds the positive and negative radicles together in a covalent molecule may be so weak as to interfere but little with the disruption of the molecule into ions, with the result that a compound of the second type may exhibit the behaviour of a strong electrolyte.

2. *Electrolytic Dissociation of Strong Electrolytes.*

A "strong electrolyte" means, in the first instance, nothing more than a substance which has a high electrolytic conductivity, *e. g.*, in aqueous solutions. In the language of Arrhenius's theory, such a substance was said to have a large "coefficient of ionization"; but this term has no longer any real meaning when applied to a salt which is 100 per cent. ionized even in the solid state. We can, however, still interpret the decrease of equivalent conductivity in strong solutions as being due, at least in part, to the formation of electrically-neutral doublets, which play the part of molecules, just as in the vapour of the salt. We need, therefore, only modify Arrhenius's equation to the extent of writing

$$\overset{+}{\mathrm{Na}}\overset{-}{\mathrm{Cl}} \rightleftharpoons \overset{+}{\mathrm{Na}} + \overset{-}{\mathrm{Cl}} \text{ instead of } \mathrm{Na-Cl} \rightleftharpoons \overset{+}{\mathrm{Na}} + \overset{-}{\mathrm{Cl}}.$$

The "degree of dissociation" of the doublets then has still a perfectly definite physical meaning, even if it cannot be calculated directly, as was formerly supposed, from the simple equation $\alpha = \Lambda/\Lambda_\infty$. Moreover, since the readiness with which neutral doublets of oppositely charged ions are

formed by the mutual attraction of their electrostatic charges must vary with the linear dimensions of the ion, with the dielectric constant and other properties of the solvent, and with the extent to which the naked ion becomes hydrated or solvated in solution, as well as with the temperature at which the association and dissociation of the ions takes place, there is ample scope, even in the theory of complete ionization, for variations in the "degree of dissociation" of different salts, either in solution or in the fused state.

(a) *Ionization of Strong Electrolytes in Solution.*—Is it possible, then, for a completely ionized salt to behave as a "weak electrolyte" and exhibit a low "coefficient of ionization" or, more accurately, a low "degree of dissociation" of the pre-existing ions? The answer is undoubtedly "Yes," provided always that the conditions under which this effect is theoretically possible can be realized in practice.

Of these conditions the most obvious has reference to the nature of the solvent. Thus Hartley* has shown that, in the case of N/500 KI, the ratio Λ/Λ_∞ falls from 0·98 in water to 0·90 in methyl alcohol, 0·81 in ethyl alcohol and 0·77 in acetone, although his solutions were all so dilute that $1-\alpha$ was still proportional to the square root of the concentration as required by the theory of complete ionization. If, then, we accept the general validity of Walden's rule, that *a dissolved salt gives a definite value for* Λ/Λ_∞ *at a dilution which is inversely proportional to the cube of the dielectric constant of the solvent*, it follows that we should be able to repress the dissociation of the ions to any desired extent by dissolving the salt in a medium of low dielectric-constant.

At this point, however, a fresh difficulty presents itself, since the majority of metallic salts are insoluble except in media which possess marked ionizing properties; in particular, most of these compounds are completely insoluble in media, such as benzene or cyclohexane, where the dielectric constant is low enough to compel the salt to behave as a weak electrolyte. Walden has, indeed, put forward a definite rule, according to which *the coefficient of ionization of a salt is approximately constant for saturated solutions in any anhydrous solvent.* Thus in the case of tetraethylammonium iodide, we should not expect to find any solution in which the "degree of dissociation" is much below 50 per cent., since saturated solutions in a dozen different solvents (but excluding water

* 'Nature,' cxix. p. 323 (Feb. 26, 1927).

and all other solvents in which the solubility is more than 1 gram-molecule in 2500 c.c.) gave values for $\alpha = \Lambda/\Lambda_\infty$ which were almost constant at 0·48. We may therefore conclude that only in exceptional cases will it be possible to prepare a solution of a strong electrolyte in which the degree of dissociation is so small as to be negligible, and that this effect, when it occurs, will probably be due to some special chemical relationship between the solvent and the solute, which enables the solute to dissolve, but without any marked disruption of the ions.

Such an effect might be looked for in Reychler's trimethylcetylammonium cetylsulphonate

$$C_{15}H_{31}.\overset{+}{N}Me_3\,|\,\overset{-}{O}.SO_2.C_{15}H_{31},$$

in which the single polar valency in the middle of so long a chain of atoms might very well remain almost undetected. Thus, whilst the 30 carbon atoms in the two hydrocarbon chains should suffice to make the compound soluble in hydrocarbon solvents, these solvents need not necessarily be so drastic in their action as to tear the two ions apart. Fortunately, however, this phenomenon can be observed in much simpler compounds. Thus, sodium oleate at a dilution of 100 litres gives the following equivalent conductivities in water and in methyl, ethyl, and amyl alcohols:—

H_2O	CH_3OH	$C_2H_5.OH$	$C_5H_{11}.OH$
$\epsilon=81·7$	$\epsilon=35·4$	25·4	15·9
$\Lambda_{100}^{18}=30·09$	$\Lambda_{100}^{25}=0·0052$	0·0018	0·0002

When sodium oleate is dissolved in *water*, the "hydrophilous" sodium ion compels the "anhydrophilous" oleate ion to follow it into aqueous solution, where it functions as the "ionic micelle" of a "colloidal electrolyte." In the alcohols, on the other hand, and especially in amyl alcohol, the oleate radicle appears to drag a reluctant sodium ion into solution in *an organic solvent, in which the salt behaves for all practical purposes as a non-electrolyte.*

Walden, however, has gone a great deal further in studying the abnormal conductivities of salts in hydrocarbons and in their halogen derivatives. Thus, by a suitable choice of radicles, in salts such as $\overset{+}{N}(C_5H_{11})_4\overset{-}{I}$, he has been able to obtain solutions of reasonable strength in a dozen of the least promising solvents, including benzene and toluene, methyl iodide, methylene and ethylene chlorides, chloroform and carbon tetrachloride. In every case, the salt-solution

showed an appreciable conductivity, the values for Λ_{20}^{25} varying from 0·0140 in carbon tetrachloride to 1·57 in chloroform and 9·51 in methylene chloride; but the equivalent conductivities were abnormal in that they generally fell to a minimum value at some intermediate dilution, from which there was not only the usual increase on dilution, but an equally striking increase on passing to more concentrated solutions. The "degree of dissociation" was obviously small and in some cases almost negligible, so that the "salt" was behaving quite clearly as a "weak electrolyte" in all these solvents. Neutralization of the ionic charges, however, would appear to be even more difficult than usual, in view of the fact that the positively-charged nitrogen of the tetra-amylammonium ion is separated from the negatively-charged halogen ion by a permanent hydrocarbon "atmosphere" containing 20 atoms of carbon. The small conductivity of these solutions then suggests that the salt must be present predominantly in the form of neutral ionic doublets, rather than as freely dissociated ions. The formation of these doublets also appears to afford a sufficient explanation of the different absorption-coefficients which Hantzsch observed * when quaternary ammonium salts of this type were dissolved in organic solvents instead of in water, since we need not suppose that the absorption-coefficients of the ionic doublet must necessarily be identical with those of the aqueous ions.

Attention may also be directed to the fact that, whilst solutions of phosphorus pentabromide and antimony pentabromide in liquid bromine exhibit a marked conductivity †, the equivalent conductivity decreasing with dilution just as in the case of the "abnormal" conductivities cited above, potassium bromide and tetramethylammonium iodide, as well as tribromacetic acid, behave as insulators in this solvent (Walden).

(b) *Ionization of Fused Salts.*—Since considerations of limited solubility do not apply in the case of fused salts, it is of special interest to inquire what is known in reference to the magnitude of the "degree of dissociation" under these conditions. It has been generally assumed that the calculation of these coefficients is impossible, since it cannot be done either by Arrhenius's method, which depends on measuring the conductivity of the salt at different stages of dilution with a solvent, or by van't Hoff's method, which implies

* *Ber.* lii. p. 5444 (1919).

† Plotnikow, *Z. physikal. Chem.* xlviii. p. 228 (1904).

a knowledge of the osmotic pressure of the salt in solution. A formal solution of the problem is possible, however, in the case of fused silver chloride at 600° C., for which the relevant data are all known, namely,

Molecular weight	$M=143{\cdot}34$.
Density.....	$\delta=5{\cdot}267-0{\cdot}0092t=4{\cdot}715$ at 600°.
Specific conductivity	$\kappa=4{\cdot}48$ at 600°.
Viscosity	$\eta=0{\cdot}01606$ at 603°.

The normality of the fused salt is $4715\div143{\cdot}34=32{\cdot}9\text{N}$; and the equivalent conductivity is therefore $\Lambda=4{\cdot}48\div0{\cdot}0329=136$. The limiting value for the conductivity at infinite dilution in aqueous solution is given by the sum of the ionic mobilities as $54+65=119$; if, therefore, a proportional allowance is made for an increase of viscosity from 0·01056 to 0·01606, the corresponding limiting value for the fused salt would be $\Lambda_\infty=119\times0{\cdot}01056\div0{\cdot}01606=78$. The equivalent conductivity of a completely ionized salt can, however, also be calculated, without making use of the value for aqueous solutions, by means of Walden's relation, $\Lambda_\infty\eta_\infty\sqrt{\text{M}}=11{\cdot}15$, which has been verified for six salts in 29 non-aqueous solvents, as well as for two "anhydrous" salts in aqueous solution. For silver chloride this relation gives $\Lambda_\infty=11{\cdot}15\div0{\cdot}01606\div12=58$.

These two methods of calculation concur in giving a maximum conductivity for completely dissociated silver chloride, $\text{AgCl}\rightarrow\overset{+}{\text{A}}\text{g}+\overset{-}{\text{Cl}}$, which is only about half as great as the values found experimentally. It has been suggested, and the idea has found widespread acceptance, that the exceptional mobility of the ions $\overset{+}{\text{H}}$ and $\overset{-}{\text{OH}}$ in aqueous solutions is due to the fact that they are *the ions of the solvent*. This idea is at least plausible in the case of water, where it might be supposed that the exceptional mobility of $\overset{+}{\text{H}}$ (in the form of $\overset{+}{\text{O}}\text{H}_3$, since $\overset{+}{\text{H}}$ cannot persist as a separate entity), depended in part on the transfer of a naked proton from one complex to another, without necessarily involving the migration of the whole of the oxonium ion; but it is not valid, even in the closely-related case of liquid ammonia, where $\overset{+}{\text{H}}$ (in the form of $\overset{+}{\text{N}}\text{H}_4$) and $\overset{-}{\text{N}}\text{H}_2$ are less mobile than $\overset{+}{\text{K}}$ and $\overset{+}{\text{Tl}}$; and there is no reason why it should be true in the case of a completely ionized salt, where it is

difficult even to suggest a theoretical justification for it. It therefore appears more likely that the high conductivity of fused silver chloride may be due to the presence of something analogous to the "ionic micelle" in a colloidal electrolyte, *i. e.*, to complex aggregates of ions carrying multiple electric charges, since these would have the effect of increasing both the viscosity and the electrolytic conductivity of the melt. Such aggregates might be formed by an incomplete destruction of the crystal lattice, and it may be supposed that the conductivity of a fused salt is determined very largely by the character of the aggregates that persist when the crystalline salt is melted.

From this point of view it is of interest to notice that all fused salts are not good electrolytes, even when the theory of valency indicates that they must be completely ionized. Thus, leaving out weak electrolytes such as $SnCl_4$ and $HgCl_2$, where covalent molecules appear to be formed from the metal and the halogen, the values

$$\Lambda^{70}=0{\cdot}0009,\ \Lambda^{100}=0{\cdot}0050$$

recorded by Walden for the molten hydrobromide of dimethyl-aniline, present a remarkable contrast with the values

$$\Lambda^{600}=4{\cdot}48,\ \Lambda^{800}=4{\cdot}98$$

for silver chloride. In this compound we must either suppose that the fused solid breaks up into electrically neutral doublets, $[\overset{+}{\mathrm{N}}\mathrm{HPhMe_2}\,|\,\overset{-}{\mathrm{Br}}]$, in which the oppositely-charged ions cling together, just as they must do in a salt-vapour of normal vapour-density, and, therefore, do not migrate in opposite directions under the influence of a small electromotive force; or we must postulate the existence of some subtle type of bond, which binds the ions into a molecule of such an unstable character that it is unable to persist in aqueous solution*. Until, however, the existence of such molecules has been proved, it is simpler to admit that a salt, even if it is completely ionized in the crystalline state, will not become a good electrolyte when fused, unless the lattice is resolved into oppositely-charged fragments. If the cleavage of the lattice on fusion tends predominantly to produce neutral ionic aggregates like those which are formed on vaporization, the conductivity of the fused salt may be reduced to such an extent as to give rise to the properties of

* Compare Hantzsch's hypothetical pseudo-ammonium halides; also Ulich, Trans. Faraday Soc. 1928.

a typical "weak electrolyte." This effect, it is clear, is most likely to appear in salts which are easily vaporized, *i. e.*, which break down readily into volatile neutral doublets.

3. *Hydrolysis.*

It is an interesting and novel feature of the theory of complete ionization that it very largely destroys the meaning of the term "hydrolysis." Thus an equation such as

$$\overset{+}{\mathrm{N}}\mathrm{a}\overset{-}{\mathrm{Cl}} + \mathrm{HOH} \rightleftharpoons \overset{+}{\mathrm{N}}\mathrm{a}\overset{-}{\mathrm{O}}\mathrm{H} + \overset{+}{\mathrm{H}}\overset{-}{\mathrm{Cl}}$$

becomes a mere paraphrase of the equation

$$\mathrm{HOH} \rightleftharpoons \overset{+}{\mathrm{H}} + \overset{-}{\mathrm{O}}\mathrm{H},$$

unless we admit that the theory of complete ionization breaks down in the case of one or both of the products.

This can always be admitted in the case of the acid, since all hydrogen compounds exist predominantly in a covalent form. A more curious case is afforded by ammonium chloride,

$$[\overset{+}{\mathrm{N}}\mathrm{H}_4]\overset{-}{\mathrm{Cl}} + \mathrm{HOH} \rightleftharpoons [\overset{+}{\mathrm{N}}\mathrm{H}_4]\overset{-}{\mathrm{O}}\mathrm{H} + \overset{+}{\mathrm{H}}\overset{-}{\mathrm{Cl}},$$

where the *acid* is so strong that the proportion of covalent hydrogen chloride is too small to produce an appreciable vapour-pressure, but where the *base* is quite weak, so that hydrolysis must depend on the conversion of ammonium hydroxide into a covalent compound. This may take place, as Latimer and Rodebush have suggested *, through the weak linkage of a bivalent hydrogen atom

$$\overset{+}{\mathrm{N}}\mathrm{H}_4 + \overset{-}{\mathrm{O}}\mathrm{H} \rightleftharpoons \mathrm{NH}_3\,.\,\mathrm{H}\,.\,\mathrm{O}\,.\,\mathrm{H}.$$

A more familiar, but less effective, method is by eliminating the hydroxyl ion as a covalent molecule of water,

$$\overset{+}{\mathrm{N}}\mathrm{H}_4 + \overset{-}{\mathrm{O}}\mathrm{H} \rightleftharpoons \mathrm{NH}_3 + \mathrm{H}_2\mathrm{O}.$$

In the latter case the *hydrolysis* of the salt of a weak ammonium base (which would then be a thermal dissociation into which water does not enter directly,

$$\overset{+}{\mathrm{N}}\mathrm{H}_4\overset{-}{\mathrm{Cl}}\,\mathrm{aq} \rightleftharpoons \mathrm{NH}_3\,\mathrm{aq} + \mathrm{HCl}\,\mathrm{aq})$$

would actually depend on a *dehydration* of the hydroxide.

* J. Am. Chem. Soc. xlii. p. 1431 (1920); *cf.* Moore & Winmill, J. Chem. Soc. ci. p. 1675 (1912).

A similar example of "hydrolysis by dehydration" is afforded by the quinquevalent compounds of phosphorus, arsenic, and antimony *. Thus trimethylstibine dibromide can be hydrolysed in two stages as follows:—

$$SbMe_3Br_2 \rightarrow SbMe_3(OH)Br \rightarrow SbMe_3O$$

or $$[\overset{+}{S}bMe_3Br]\overset{-}{B}r \rightarrow [\overset{+}{S}bMe_3OH]\overset{-}{B}r \rightarrow [\overset{+}{S}bMe_3\overset{-}{O}].$$

In the first stage, hydrolysis can take place in the normal way, by an interchange of Br and OH, since the hydroxyl-ion of the base can be fixed by the quadricovalent antimony, giving rise to a product which can be isolated in the form of an oxy-bromide, $\overset{-}{B}r[\overset{+}{S}bMe_3 . O . \overset{+}{S}bMe_3]\overset{-}{B}r$; but, since the equation

$$[\overset{+}{S}bMe_3OH]\overset{-}{B}r + \overset{+}{K}\overset{-}{O}H \rightleftharpoons [\overset{+}{S}bMe_3\overset{-}{O}H]\overset{-}{O}H + \overset{+}{K}\overset{-}{B}r$$

has no meaning, from the point of view of the theory of complete ionization, the second stage of the hydrolysis must depend on a direct removal of HBr, giving rise to an oxide, which can be isolated without difficulty, instead of to a dihydroxide.

Summary.

(*a*) Compounds in which neutralization of the ionic charges is prevented by the laws of valency generally behave as "strong electrolytes" in solution. Badly-conducting solutions can, however, be obtained by dissolving a salt in a medium with a low dielectric constant, when abnormal variations of conductivity with dilution are generally observed.

(*b*) Many fused salts are good conductors, giving values for the "coefficient of ionization" which may be above 100 per cent., perhaps as a result of the formation of multiple-charged ionic aggregates. Other fused salts, however, are poor conductors, probably because the crystal lattice breaks down into neutral ionic doublets on fusion.

(*c*) The term "hydrolysis" has no significance, from the point of view of the theory of complete ionization, unless the hydrogen or hydroxyl ion of water can be fixed by one of the ions of the salt, with formation of a covalent compound.

* Hantzsch & Hibbert, *Ber.* xl. p. 1513 (1909).

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CIX. *Note on the Diffusion of Hydrogen through Iron.*

By W. Edwards Deming *.

THE diffusion of gases through metals has called forth no little theoretical and experimental work, chiefly since 1904, with the impetus given by the brilliant papers of Richardson[1], and Richardson, Nicol, and Parnell[2]. In the former is derived an expression for the rate of flow for a gas through a slab of thickness x and with gas pressures P_1 and P_2 on its sides. When the gas does not combine chemically with the material through which it is passing, this expression is the sum of two terms, one proportional to $(P_2-P_1)x^{-1}$, and the other to $(P_2^{1/n}-P_1^{1/n})x^{-1}$, *i.e.*, to the concentration gradients of the undissociated and of the dissociated gas. (n is here the number of atoms into which one molecule of the gas dissociates, according to $X_n \rightleftharpoons nX$). It was expected that in metals the former term would be inappreciable compared with the latter, one reason being that in these substances dissociation of a gas into atoms is believed to be readily accomplished. An abundance of experimental work has confirmed this expectation ; for example, Richardson, Nicol, and Parnell[2], and more recently Lombard[3, 4, 5] found that the diffusion rate of hydrogen through iron and other metals is proportional to $P^{\frac{1}{2}}$ (the pressure being zero on the low-pressure side). Substantially the same is concluded by Borelius[6], whose work will be mentioned later in another topic. But through rubber and fabric, Edwards and Pickering[7] found the rate of diffusion of any gas to be proportional to its partial pressure if the total pressure remains constant.

The conclusions of experimenters, that the amount m of hydrogen passing through an iron (or other metal) slab of thickness x in a time t is proportional to $P^{\frac{1}{2}}$, are quite unanimous, but, owing to the fact that the pressure on the low-pressure side has in every experiment (as far as the writer can ascertain) been zero, it is impossible to tell whether their data confirm

$$m = K_1 A t \frac{(P_2^{1/n}-P_1^{1/n})}{x^{\alpha_1}}, \quad . \quad . \quad . \quad . \quad (1)$$

or

$$m = K_2 A t \frac{(P_2-P_1)^{1/n}}{x^{\alpha_2}}, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

because both of these reduce to $m \propto P^{1/n}$ when $P_1=0$ and x is kept constant.

* Communicated by the Author.

Nearly all experimenters on the subject have investigated the variation of the diffusion rate with pressure and temperature, few its variation with thickness. The writer wishes to show that experiments on the variation of diffusion rate with respect to thickness of a metal will enable us to decide between these two equations, for, as will be proved shortly, α_1 must be unity and α_2 must be $1/n$. Hence the fact that Lombard [4] found the diffusion rate of hydrogen through metals to vary inversely as the thickness is experimental proof not only that $m \propto x^{-1}$, but also decides in favour of $m \propto (P_2^{1/n} - P_1^{1/n})$ rather than $m \propto (P_2 - P_1)^{1/n}$. On the other hand, the fact that Edwards and Pickering [7] found $m \propto x^{-1}$ for hydrogen passing through rubber was to be expected, because if $n=1$, as their conclusion $m \propto P$ for rubber indicates, then (1) and (2) become identical.

To investigate α_1 and α_2, imagine a plane slab of homogeneous material of thickness a with pressures P_1 and P_2 on its sides. Let the two faces of an infinitesimal slice be distant x and $x+dx$ from the side whose pressure is P_1, and let the pressures with which these two faces are in equilibrium when the steady state is reached be y and $y+dy$. (1) demands that

$$\frac{(y+dy)^{1/n} - y^{1/n}}{(dx)^{\alpha_1}} = \frac{y^{1/n} - P_1^{1/n}}{x^{\alpha_1}}$$

$$\frac{d(y)^{1/n}}{(dx)^{\alpha_1}} = \frac{y^{1/n} - P_1^{1/n}}{x^{\alpha_1}}.$$

Clearly α_1 must be unity, because $dy^{1/n}$ and dx are the same order of infinitesimals. With $\alpha_1 = 1$, this integrates to

$$y^{1/n} = (P_2^{1/n} - P_1^{1/n}) x/a + P_1^{1/n};$$

and, more important, (1) yields for the amount dm of hydrogen diffusing through an area A of thickness dx, with pressures P and $P+dP$,

$$dm = K_1 A \nabla P^{1/n}\, dt, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in time dt. So, if experimenters using $P_1 \neq 0$ and $P_2 \neq 0$ find either $m \propto (P_2^{1/n} - P_1^{1/n})$ or $m \propto x^{-1}$ for a plane slab, then (1) is established and (3) would be the differential equation to be applied to any problem of diffusion through walls of any shape, plane slab, cylindrical shell, spherical shell, etc., in the steady state.

By similar reasoning with (2), α_2 must be $1/n$, and at any point x in the slab

$$y = (P_2 - P_1) x/a + P_1,$$

(2) yields

$$dm = K_2 A (\nabla P)^{1/n}\, dt. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Now if it is found either that $m \propto (P_2 - P_1)^{1/n}$ or that $m \propto x^{-1/n}$, then (2) would be established and (4) would be the proper differential equation for the steady state.

Borelius[6] finds the amount of hydrogen absorbed or in solution in metals to be proportional to the square root of the pressure to which the metal is subjected. He substantiates this with some theory. If his result is correct, then equation (3) means that the amount of hydrogen diffusing normally through any (small) area would be proportional to the concentration gradient at that point, a logical supposition. Lombard[5], working with a slab of electrolytic iron at 300° C., thickness 0·0162 cm., $P_2 = 1$ atmosphere, $P_2 = 0$, found dm/dt to be 5·62 c.c. of hydrogen (S.T.P.) per hour, whence $K_1 = 0{\cdot}091$, and $K_2 = 0{\cdot}715$ in the same units. Dr. E. P. Bartlett, of this Laboratory, has recently extended his pressure, volume, and temperature relations[8] to 400° C. For this work he employed a chrome vanadium steel pipet seven inches long and having internal and external radii $\frac{1}{8}$ inch and $\frac{9}{8}$ inch. At $P_2 = 1000$ atmospheres and $P_1 = 0$, he observed 0·5 c.c. of hydrogen (S.T.P.) diffusing through the walls per hour. Equation (3) applied to a seven-inch portion of an infinitely long cylinder (the end correction being an unnecessary refinement) yields the result 2·5 c.c. of hydrogen (S.T.P.) per hour, and equation (4) yields 25 c.c. per hour, using $K_1 = 0{\cdot}091$ and $K_2 = 0{\cdot}715$. Naturally one would expect the K_1 or K_2 to be several times less for chrome vanadium steel than for electrolytic iron, so it may be concluded from this that equation (3) gives fairly good results up to very high pressures, and that equation (4) is not valid.

Adopting (3), and with Borelius taking the solubility proportional to the square root of the subjecting pressure, it is easy to extend the equation to apply at any time, whether the steady state obtains or not.

$$\frac{dP^{1/n}}{dt} = \frac{K_1}{c} \nabla^2 P^{1/n}, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

c is the amount of gas absorbed per unit volume under unit pressure. In the steady state, $dP^{1/n}/dt = 0$, and under this condition, equation (3) is a first integral of (5).

In dealing with the conduction of heat, we write

$$d\theta/dt = h^2 \nabla^2 e,$$

which is exactly in the same form for θ as (5) is for $P^{1/n}$. Thus problems in the diffusion of a gas through metals become the problems in the conduction of heat, whose solutions are now classic.

It is a pleasure to thank Dr. P. H. Emmett, of this Laboratory, for several suggestions for the presentation of these ideas.

References.

(1) Richardson, Phil. Mag. vii. p. 266 (1904).
(2) Richardson, Nicol, Parnell, Phil. Mag. viii. p. 1 (1904).
(3) V. Lombard, *Comptes Rendus*, clxxvii. p. 116 (1923); clxxxii. p. 463 (1926).
(4) V. Lombard, *Ibid.* clxxxiv. p. 1327 (1927).
(5) V. Lombard, *Ibid.* clxxxiv. p. 1557 (1927).
(6) G. Borelius, *Ann. Physik*, lxxxiii. p. 121 (1927).
(7) J. D. Edwards and S. F. Pickering, Sci. Papers, Bureau of Standards, No. 387, pp. 327–362 (1923); Chem. & Met. Eng. xxiii. pp. 17–21 and pp. 71–75 (1920).
(8) E. P. Bartlett, Journ. Am. Chem. Soc. xlix. pp. 687, 1955 (1927); and extensions of this work to appear in the May number of the same journal.

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CX. *The Emission of Particles from Hot Platinum in Air at Atmospheric Pressure.* *By* William D. Flower, *B.Sc.**.

[Plate XV.]

MEASUREMENTS of the mobility of ions emitted by hot wires at atmospheric pressure have disclosed that the emission consists initially of normal ions and uncharged nuclei. Since in the presence of ions these nuclei can pick up charges, the nature and rate of their growth is a matter of some interest, as it might lead ultimately to information on the variation of mobility with the size of the ion. It was felt that an ultra-microscopic survey of air containing these nuclei might throw some light upon the problem. Such a study of the large ions from a bunsen flame had already been made by De Broglie[2], who described the sample as nearly optically empty. Nolan and Enright[3], however, were led to the conclusion that the radius of large ions from a flame is greater than $1{\cdot}0 \times 10^{-5}$ cm., and De Broglie[4] himself, from his measurements of Brownian motion in gases, deduced a value of the order $0{\cdot}5 \times 10^{-6}$ cm.

* Communicated by Prof. A. M. Tyndall, D.Sc.

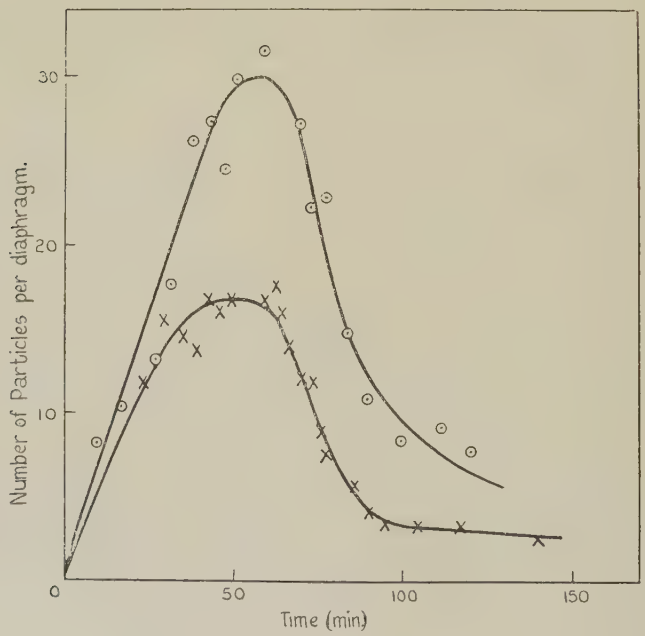
Particles of this size should be visible in the ultra-microscope. While it is conceivable that the reason for the approach to optical emptiness of the sample was that the large ions consisted of a loose grouping of molecules too diffuse to give an ultra-microscopic image, yet it might be possible to detect a greater number by improvement of the optical system. For this reason, as a preliminary, some experiments on the gases from a bunsen flame were carried out, using the ultra-microscopic method developed by Whytlaw-Gray[5] for the examination of aerosols. The apparatus used was essentially the same as that described by him, except that bilateral illumination from two 1000-c.p. pointolite lamps was used. To obtain a supply of large ions and nuclei a bunsen burner was placed in the large chamber and the atmosphere in the latter was then rendered dust free. The bunsen was lighted by an incandescent platinum spiral placed above it and allowed to burn for a few minutes. A sample of the dispersoid was then drawn off and examined in the ultra-microscope. A large number of particles, exhibiting violent Brownian movement, were observed. The same result was obtained when the coal-gas supplied to the bunsen was filtered. It was reasonable to conclude from this that with the optical arrangements described large ions were visible in the ultra-microscope.

The apparatus was then adapted for examining the emission from a hot wire by replacing the bunsen flame by a spiral of platinum wire which had been previously cleaned in acid, washed in distilled water, and dried. After the wire had been heated to a dull red heat for twenty minutes the examination of a sample showed the existence of particles, smaller in number, however, than in the preceding case.

It might be expected that the phenomenon of coagulation in aerosols would have a counterpart in these systems. To test this the following procedure was adopted. The nuclei were generated by passing a known current through the spiral for four minutes. In later work this time of generation was varied to other values and in some cases was reduced to twenty seconds. The current was switched off, the air in the chamber kept in constant circulation by a small propellor, and a very slow flow of dispersoid maintained through the observation chamber. Counts in uninterrupted succession were made of the number of particles seen through the eyepiece stops. Some typical results are shown in fig. 1 of the variation of number with time over a period of about two hours for two different values of the heating current and therefore of the temperature of the wire.

As will be shown later, the numbers recorded must be corrected because of the possibility of the inclusion in the counts in certain cases of particles lying outside the beam, but sufficiently illuminated by light scattered from particles inside the beam to be recorded as present. This, however, does not alter the general shape of the curve with its definite rise to a maximum at about one hour and its subsequent fall. The higher the temperature of the wire, the higher the maximum value becomes. It was found, however, that successive

Fig. 1.



curves for the same temperature did not repeat one another, but progressively decreased in height, indicating that the ability of the wire to emit these particles decreased with use. Further, after prolonged heating for about twelve hours, the appearance of the particles in the field of view was different from that after initial heating. The brightness of the disks decreased with succeeding curves until eventually only faint points in intense Brownian movement were observed and even these only under the best conditions. By passing

through the wire a current higher than that previously used or by heating the fatigued wire in a bunsen flame for a short time, its power of emission was temporarily restored.

This effect is analogous to the behavour of the positive ion emission from a hot filament, but as the two phenomena were not studied simultaneously, it is not possible to say whether they are in any way related.

It is possible to explain the general form of the curve in a simple manner. It may be assumed that at emission the particles, whether they are atoms, molecules, or minute particles of metal, are too small to be seen at all and therefore nothing countable is perceived in the ultra-microscope at the time when a heating current of short duration is cut off. By coagulation with one another with time they grow in size and become visible. Some grow more rapidly than others and these are seen first. At the same time it should be mentioned that the actual process of collision and coalescence of two particles was never visually observed in the field of view of the microscope.

From the quantitative side there seemed to be little hope of carrying the matter any further on these lines unless it was possible in some way to make all the particles visible at all times. If, however, one assumes that each of the particles, whatever its age, can act as a nuclei for condensation when supplied to a Wilson expansion chamber this result can be achieved.

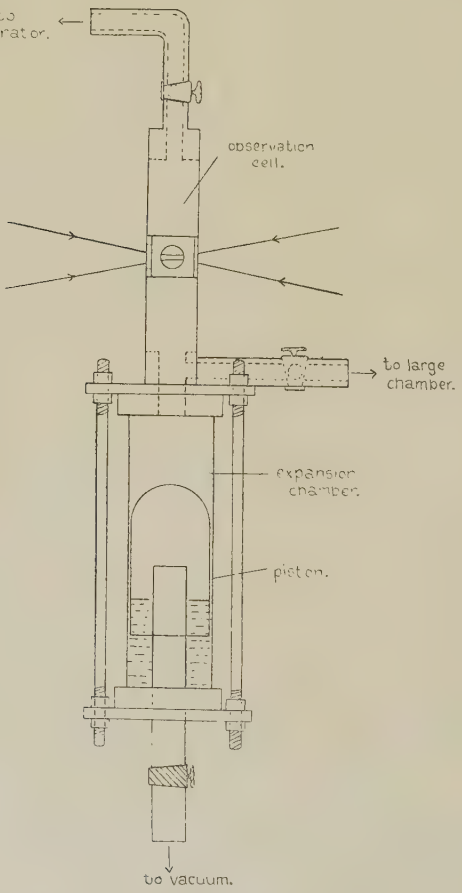
The form of apparatus used was such that the observation cell formed part of the expansion chamber and is shown diagrammatically (fig. 2). A given height of the piston corresponded to a certain expansion ratio which could be determined by calibration. It was found unnecessary to use an expansion ratio greater than 1·3, since there was no increase in the number of particles seen when a greater ratio than this was used.

In the following experiments the nuclei were produced in exactly the same manner as before. In order to determine the number of nuclei per unit volume the number of particles seen in the eyepiece stop of the microscope, directly after producing an expansion, was noted. Owing to the fact that the cloud formed fell rapidly, under the action of gravity, considerable practice was required in estimating the number of particles seen. Typical results obtained by this method are shown graphically in fig. 3 for two experiments.

It will be seen from curves A_1, A_2, that the number of

particles is now shown to be a maximum at zero time and to diminish subsequently along a hyperbolic curve. This is shown by plotting the particulate volume with time, curves B_1, B_2.

Fig. 2.

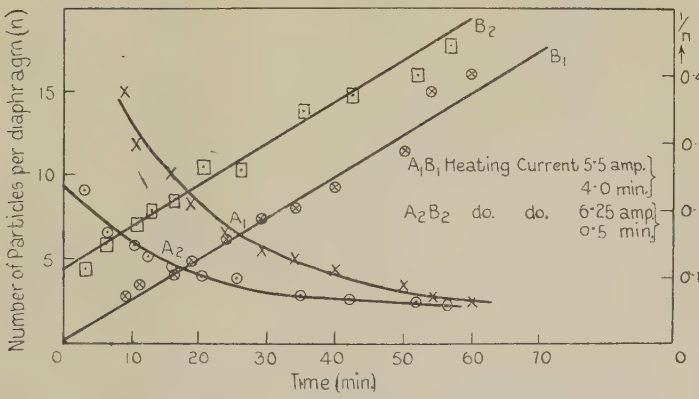


It would appear at first sight that it would be a simple matter to express these results quantitatively in terms of the number of particles per unit volume, provided that the depth of the illuminated beam is known, but, as Whytlaw-Gray has pointed out, the difficulty is found in this form of

observation cell * in making accurate measurements of the depth of the beam since the edges of the beam were not clearly defined owing to the light scattered or reflected from particles inside the beam illuminating them outside. An error was thus introduced in calculating the absolute number per unit volume. Further, as the system aged, the number of particles in the field of view decreased and it became necessary to change from one eyepiece stop to another. It was found that the number counted was not proportional to the change in area, the number with the larger stop being smaller in proportion than with the smaller one.

At this stage the writer was brought into touch with Mr. Green, who was working on similar lines on the coagulation of smoke particles, and from this point the work was

Fig. 3.



continued in consultation with him. He had experienced the same difficulties on the quantitative side and in order to overcome them had developed a photographic method in conjunction with a continuous action Wilson apparatus [7]. In this method a photograph was taken of the contents of the cell immediately after an expansion and the resulting negative counted under a reading microscope. Mr. Green kindly allowed his apparatus to be used by the writer and with it a series of experiments was carried out. The results for two experiments are collected below, Table I., and shown graphically in fig. 4.

* In later work by Whytlaw-Gray [6] this has been avoided by using a different type of cell.

TABLE I.

Experiment B 3.

Heating Current ..... 6·53 amp.
Duration of Heating Current ..... 2·0 min.

Time T min.	No. of Nuclei per c.c. N.	Particulate Volume I/N.
1·50	$30{\cdot}80 \times 10^4$	$3{\cdot}25 \times 10^{-6}$
4·25	28·55	3·52
8·25	25·10	3·98
13·60	24·30	4·12
15·20	21·30	4·59
17·20	22·18	4·54
20·75	21·70	4·61
29·25	19·20	5·21
33·00	18·00	5·56
36·50	15·92	6·30
40·20	17·10	5·85
44·50	15·32	6·54
48·25	14·73	6·82
50·50	14·49	6·99
56·35	14·20	7·04
59·35	12·90	7·75
63·40	11·33	8·87
66·00	11·70	8·55
71·50	11·33	8·87
74·80	10·33	9·73
79·00	9·52	10·50
81·10	10·55	9·57
89·00	9·32	10·72

Experiment B 4.[1]

Heating Current ..... 7·0 amp.
Duration of Heating Current ..... 2·0 min.

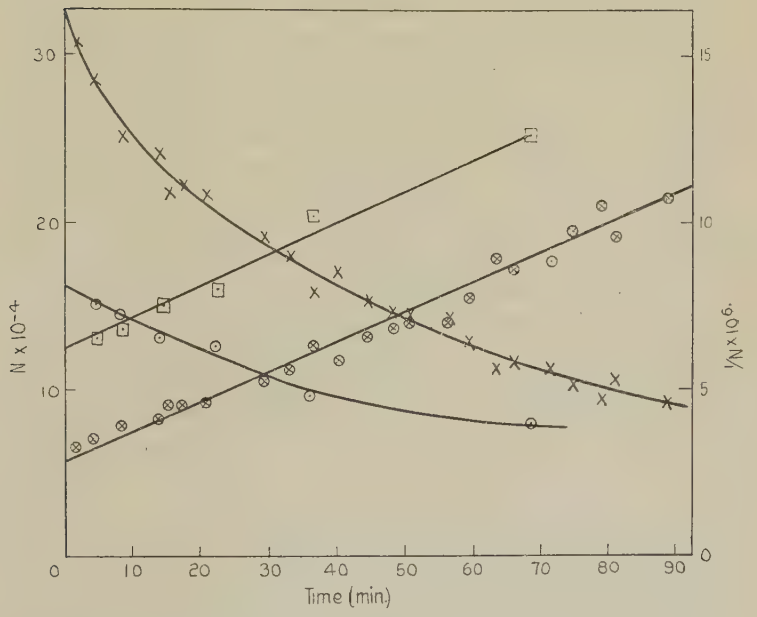
4·5	15·10	6·6
8·0	14·50	6·9
14·0	13·08	7·6
22·0	12·50	8·0
36·0	9·78	10·2
68·5	7·95	12·6

[1] Enlargements from photographs taken during Experiment B 4 are given on Plate XV.

To test whether these nuclei were charged a cylindrical ionization chamber was introduced between the observation cell and the metre chamber. The electric field and the rate of flow through the ionization chamber were so adjusted

that only ions of mobility less than $3{\cdot}5 \times 10^{-5}$ cm./sec./volt/cm., could pass through to the cell. It was found that in an aerosol of nuclei emitted from a hot platinum wire the majority of particles were initially uncharged but that more charged particles made their appearance during the stages of coagulation so that after a period of about sixty minutes half of the total number of nuclei present were charged.

Fig. 4.



The Accuracy of the Observations.

The question of the probable error in the observations has been considered on the same lines as has been done by Green, and suggests that the irregular variations shown by the departure of many of the points from the mean straight line is consistent with a random distribution of the nuclei.

Discussion of Results.

The number-time curves showing the variation of the total number of nuclei with time, for both the visual and photographic methods, exhibit certain characteristics in common. They all show a decrease in number of nuclei

with time in accordance with a hyperbolic law. This may be clearly seen by plotting the reciprocal of the number of nuclei with time when a straight line is obtained. If $n_0 =$ number of nuclei present initially, $n =$ number of nuclei present at any subsequent time t, the following relation must hold :—

$$1/n - 1/n_0 = kt \text{ or } \frac{dn}{dt} = -kn^2$$

where k is a constant.

This relation has the same form as that found by Kennedy [8] to apply to the decrease in number of large ions and nuclei from a bunsen flame.

The values of the constant k deduced from the results obtained by the photographic method are given in Table II.

Table II.

Duration of Emission in minutes.	Heating Current amp.	Number of particles per c.c. initially.	k cm.^{3}/sec.	Mean k cm.^{3}/sec.
2·0	5·7	$0{\cdot}98 \times 10^5$	$0{\cdot}15 \times 10^{-8}$	
2·0	7·0	1·10	0·16	
2·0	6·5	3·28	0·14	
2·0	7·0	1·62	0·16	$0{\cdot}15 \times 10^{-8}$
4·0	5·6	2·78	0·13	
2·0	4·8	1·88	0·13	
4·0	6·4	1·79	0·16	

If in the visual method the assumption is made that the depth of beam through which observations are made is actually the "depth of focus" of the viewing microscope, and from this calculate the number of particles per unit volume it is found that the value of k by this method is $0{\cdot}10 \times 10^{-8}$ cm.^{3}/sec. Since this number is of the same order it may be regarded as a reasonable confirmation of the value given by the photographic method.

It is interesting to compare this value with that obtained by Kennedy for the decrease in number of large ions and nuclei from a bunsen flame with time. Kennedy used an Aitken Dust-Counter and obtained the value $0{\cdot}13 \times 10^{-8}$ cm.^{3}/sec. The agreement for these two sources is satisfactory.

The only theoretical formula relating to coagulation appears to be the one derived mathematically by Smoluchowski [9] for

the coagulation of sols. In this formula $n = n_0/(1+kt)$ where n, n_0, t, and k have the same meanings as before. Also $k = 4\pi DR_a$, where D and R_a are respectively the diffusion constant and radius of the sphere of action for the same particle.

The application of the formula to the problem is only strictly justified if k is independent of n_0. Evidence of this is given in fig. 4, where the values of the particulate volume, $1/n$, are plotted against time for two experiments and the two straight lines are seen to be approximately parallel.

Whytlaw-Gray has shown from the formula that $k = 1{\cdot}46 \times 10^{-10}(1 + 9 \times 10^{-6} r^{-1}) R_a r^{-1}$ cm.^{3}/sec. It is necessary to apply the Cunningham correction to the term for the mobility of the particles involved in the diffusion constant, though this makes k a function of the initial radius of the particle. No evidence of this exists in the present experiments, though it might appear if it had been possible to study the coagulation over shorter and longer time: while therefore there is no real justification for deducing the radius of the initial nucleus from the above expression and the observed value of k, it may be of interest to note that the radius obtained in this way, $2{\cdot}2 \times 10^{-6}$ cm., lies between the value suggested by De Broglie [4] and that suggested by Nolan and Enright [3].

Summary.

An ultra-microscopic study of air containing large ions and nuclei emitted by a hot platinum wire has been made. After the source of nuclei had been removed the number visible increased to a maximum and then diminished. This is explained if at emission the nuclei are too small to be seen but subsequently coagulate.

Reliable results on the rate of coagulation of these nuclei were obtained by using them as nuclei for condensation and photographing the droplets formed.

The equation of the coagulation time-curves are hyperbolic and is given by $\frac{dn}{dt} = -kn^2$ where n is the number present and k is a constant equal to $0{\cdot}15 \times 10^{-8}$ cm.^{3}/sec. This value is in reasonable agreement with the value $0{\cdot}13 \times 10^{-8}$ cm.^{3}/sec. obtained by Kennedy for large ions and nuclei from a bunsen flame.

The application of the coagulation theory of Smoluchowski to these results is discussed.

In conclusion I wish to express my indebtedness to Professor A. M. Tyndall both for proposing the research and for the interest he took in the progress of the work, and to Mr. H. L. Green for the use of his apparatus in the latter part of the investigation.

References.

(1) Tyndall, A. M., and Grindley, G. C., Phil. Mag. xlvii. p. 701 (1924).
(2) De Broglie, *C. R.* cxlviii. p. 1317 (1909).
(3) Nolan, J. J., and Enright, J., Proc. Roy. Irish Acad. A, vi. p. 105 (1923).
(4) De Broglie, *loc. cit.* p. 1317.
(5) Whytlaw-Gray, R., and others, Proc. Roy. Soc. A, cii. p. 600 (1923).
(6) Whytlaw-Gray, R., Nonhebel, G., and others, Proc. Roy. Soc. A, cxvi. p. 540 (1927).
(7) Green, H. L., Phil. Mag. ser. 7, iv. No. 25, p. 1046 (1927).
(8) Kennedy, H., Proc. Roy. Irish Acad. A, xxxiii. p. 66 (1916).
(9) Von Smoluchowski, *Zeit. f. Phys. Chem.* xcii. p. 129 (1918).

CXI. *A Note on the Predicted Ionization Potential of Niton.* *By* Sushil Chandra Biswas, *M.Sc.**

IONIZATION potentials of elements of the same family are in general found to diminish almost in a linear way with progressing atomic number. On a closer scrutiny, however, it is found that elements in the P-shell, viz. (79) Au, (80 (Hg, (81) Tl, (82) Pb, etc., indicate an appreciable increase in their ionization values. This is shown in Table I.

Table I.

Ionization Potentials (Volts) †.

N Shell.	O Shell.	P Shell.
29. Cu—7·691	47. Ag—7·542	79. Au—9·25
30. Zn—9·35	48. Cd—8·95	80. Hg—10·39
31. Ga—5·8	49. In—5·76	81. Tl—6·08
32. Ge—	50. Sn—	82. Pb—7·93
33. As—11·54	51. Sb—8·0	83. Bi—8·0±·5
36. Kr—15·3	54. Xe—11·5	86. [Nt—14·0±0·5] (cal.)

* Communicated by Prof. S. N. Bose, M.Sc.

† Foote & Mohler, 'Origin of Spectra,' 1922. Franck & Jordan, 'Anregung Von Quantensprungen,' 1926.

It thus seems that Glockler's * and Struwe's † extrapolated value of (86) niton (8–10) volts, calculated on the assumption that the same relation which holds for the first five rare gases may be extended to all six of them, and thus the ionization potential of niton must be less than that of xenon (54), may be far from truth.

Calculation of the Ionization Potential.

Moseley's Law $\frac{\nu}{R} = \left(\frac{z'}{n}\right)^2$ can be written as

$$\frac{I}{I_H} = \left(\frac{z'}{n}\right)^2, \quad \ldots\ldots\ldots \quad (1)$$

where I represents the ionization potential of an element, I_H that of a hydrogen atom, "n" representing the total quantum number, and z' effective nuclear charge for the given element.

As, according to Sommerfeld, the energy of an electron orbit can be determined by two quantum numbers n and k (radial and azimuthal quantum numbers respectively), such that the ratio between the semi-major and semi-minor axes

$$\frac{a}{b} = \frac{n}{k},$$

it can be shown that the radius of a hydrogen-like (n, k) orbit (circular) about an effective nuclear charge z'

$$a = \frac{n^2}{z'} \cdot a_H,$$

where a_H represents the radius of a (1, 1) hydrogen orbit.

Thus

$$b = \frac{n \cdot k}{z'} \cdot a_H.$$

Now, following as according to Stoner ('Magnetism and Atomic Structure,' pp. 97, 304, 1926), the mean areal velocity of the elliptic orbit

$$\frac{\pi \cdot ab}{\tau} = \frac{\pi \cdot \bar{r}^2}{\tau}$$

or
$$\bar{r}^2 = k \cdot n \cdot \frac{n^2}{z'^2} \cdot (a_H)^2 = 0{\cdot}283 \cdot k \cdot n \cdot \left(\frac{n}{z'}\right)^2, \quad \ldots \quad (2)$$

where $\bar{r}^2$. (A.U.)^2 represents the mean square radius of (n, k)

* Glockler, Phil. Mag. l. p. 997 (1925).

† Struwe, *Zeits. f. Phys.* xxxvi. p. 410 (1926); xxxvii. p. 859 (1926).

orbit and ($a_H = 0{\cdot}532$ A.U.) as the radius of the normal atom of hydrogen has been substituted.

By combining (1) and (2) and substituting for $I_H = 13{\cdot}54$ volts,

$$I_{(\text{volts})} = \frac{k \cdot n}{r^2} \times 3{\cdot}83. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

For elements of the same family of Mendeleef's Table, "k" remains the same, and hence it follows that the ionization potentials of elements of the same family will be inversely proportional to the square of the radius and directly to the quantum number "n."

Table II. contains atomic radii as determined from their crystal data. These indicate for elements in P-shell a noticeable diminution in their values of radii. It may also be seen that the radii of elements of the same series in O- and P-shells are very nearly the same.

TABLE II.*

Atomic radii (A.U.).

N Shell.	O Shell.	P Shell.
Cu—1·42	Ag—1·62	Au—1·60
Zn—1·33	Cd—1·52	Hg—1·41
Ga—1·26	In—1·46	Tl—1·42
Ge—1·21	Sn—1·36	Pb—1·36
As—1·25†	Sb—1·44‡	Bi—1·55§
Kr—1·985‖	Xe—2·07‖	Nt—2·05‖

The radii for the rare gas elements are those as obtained by A. F. Scott ‖, who, according to Simon ¶ and Von Simson's determination of solidified argon structure to be face-centred cubic, assumed all other inert gases to have the same structure and then computed their atomic volumes from the densities at absolute zero according to Hertz's ** calculation.

* Huggins, Phys. Rev. xxviii. (ii.) p. 1024 (1926).
† Brandt, Phil. Mag. xlvii. p. 657 (1924).
‡ James and Tunstall, *ibid.* xl. p. 233 (1920).
§ James, *ibid.* xlii. p. 193 (1923), recalculated by McKeehan, Journ. Frank. Inst. cxcv p. 159 (1923).
‖ A. F. Scott, Journ. Phys. Chem. xxx. (i.) p. 580 (1926).
¶ Simon and Von Simson, *Naturwissenschaften*, xi. p. 1015 (1923).
** Hertz, *Zeits. Anorg. Chemie*, cv. p. 171 (1919).

Radius of Niton.

From the well-known ionization potentials of rare gases, the radii as calculated by equation (3) are entered in column ii. Table III. For comparison, atomic radii, determined by Rankine * from viscosity measurements, and those of Chapman † from van der Waals' "*b*," after correcting for the recent value of Loschmidt number ($2{\cdot}705 \times 10^{19}$), are given in columns iii., iv. Radii from crystal data are also included in column v.

TABLE III.

Radii (A.U.).

i. Gases.	ii. Ionization volts.	iii. Viscosity.	iv. Van der Waals' "*b*."	v. Crystal data.	vi. Differences (v.–II.).
Ne	0·84	1·18	1·188	—	—
A.....	1·20	1·43	1·42	1·89	0·67
Kr	1·52	1·60	1·62	1·99	0·47
Xe	1·83	1·76	1·77	2·07	0·24
Nt	(1·81±·03)	(1·81–1·84)‡	1·84	2·05	0·24

Indefiniteness as to the nature of the term atomic radius even for such simple monatomic gases, becomes apparent as a comparison is made of the radii for these gases by different methods. Though the radii by any two methods are not found to agree for any element, there is in general an agreement in the results of the same series by the same method, and one series of results offers parallelism with those of other methods.

The radius of niton, as calculated by Rudorf § from the critical temperature and pressure of the gas, indicates an increase in its value from that of xenon. On the other hand, the radius of niton (column v., Table III.) determined from crystal data gives a value less than that of xenon.

Though it may thus appear doubtful to extrapolate the radius of niton which may fall along the radii of other rare gases calculated from their ionization values, clearly enough the radius of this element cannot lie very far from that of xenon. It has already been noted that the radii for elements

* Rankine, Proc. Roy. Soc. A, xcviii. p. 360 (1920).
† Chapman, Phil. Trans. A, ccxvi. p. 279.
‡ Struwe, *loc. cit.*
§ Rudorf, *Zeits. f. Electro-Chemie*, xv. p. 748 (1909).

in O- and P-shells are very nearly the same, which means that, according to equation (3), the ionization values of chemically similar elements in O- and P-shells will bear a ratio as the ratio of quantum numbers 5 : 6. This is approximately satisfied from the data of ionization potentials Table I. More than that, the radius of niton is expected to be smaller than that of xenon, even from a superficial study of the radii and ionization potentials of elements in O- and P-shells (*vide* columns ii. and iii. of Tables I. and II.).

If the radius of niton is taken as 1·81 A.U., the error cannot exceed 0·03 A.U., as appears from viscosity or from critical data. Hence the calculated ionization potential of niton, taking the external electron at (6, 2) orbits is (14·0 ± ·5) volts.

Turner*, on the assumption that linear relationship subsists between the atomic numbers and quantum defects when Bohr's quantum numbers are increased by integral amounts, calculated the ionization value of niton to be (27·5 ± 1·5) volts (given the quantum number 10), but taking (n=11); the value turned so low as (4·66 ± ·11) volts. Though no satisfactory purpose is served by Turner's enumeration of quantum number, it may be seen that for (n=10), the ionization value of niton does not exceed (24·0) volts, and goes on increasing with the increase of quantum number.

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CXII. *The Shadowgraph Method as applied to a Study of the Electric Spark.* *By* Harvey A. Zinszer, *M.A., Ph.D., Professor of Physics, Hanover College, U.S.A.*†

[Plates XVI. & XVII.]

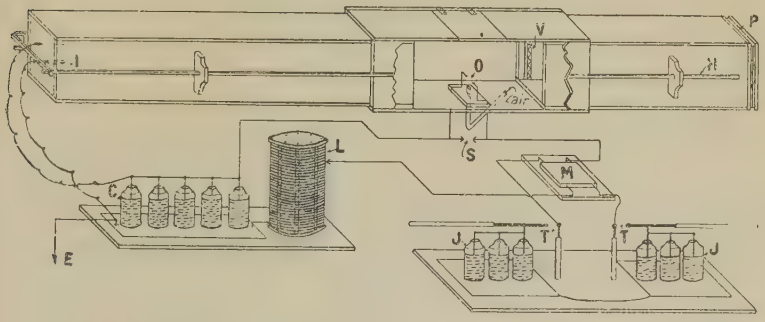
Introduction.

Ever since Henry[1] prophesied the oscillatory character of the leyden-jar discharge, a great deal of work has been done with regard to the electric spark, both from a theoretical and an engineering standpoint, and various theories of the phenomena involved in the electric spark resulting from a condensed discharge have been propounded.

* Turner, Phil. Mag. xlviii. p. 1010 (1924).
† Communicated by the Author.

Apart from the work of Fedderson [2] and Boys [3], who succeeded in photographically showing the actual oscillations in an electric spark discharge—the former by means of a rotating mirror, the latter by the use of a rotating lens system,—little work has been reported on instantaneous photographic studies of the electric-spark discharge. But as early as 1867, Toepler [4] devised the so-called "schlieren methode," a method of instantaneous photography by which he and, later, Mach [5] and Wood [6] made kinematographic demonstrations of the evolution of reflected wave-fronts resulting from spark-discharges. While their work involved the photographing of the spark itself, they were more concerned with the sound-pulse than a life-history of the spark. Moreover, their method called for a lens system which tends to mask some of the finer details of the spark

Fig. 1.



owing to the smallness of the image and the concentration of light upon the photographic plate by the lens system. In view of these facts, it was thought worth while to make a further investigation of the electric-spark discharge in order to obtain, if possible, a more complete life-history of it, and to compare the more recent theories of the spark-discharge with the photographs thus obtained.

Apparatus.

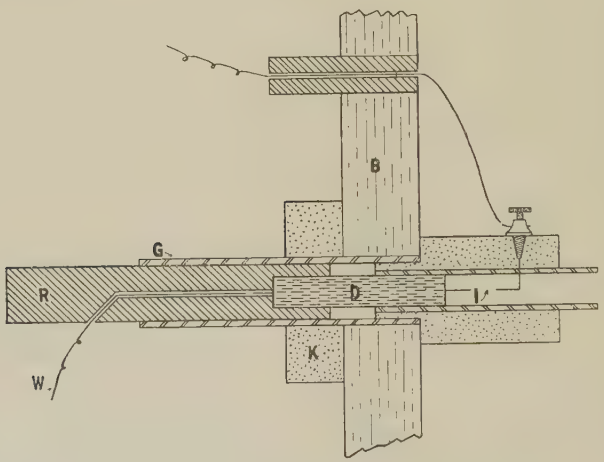
The apparatus employed in this investigation, and the operation thereof, was essentially the same as that devised by Foley and Souder [7] in their work, "A new Method of Photographing Sound-waves." The general arrangement of the apparatus in this experiment is shown in fig. 1.

The charge which produced the electric spark was generated by a Wagner static induction machine consisting of four

mica plates, 77 cm. in diameter, driven by a variable-speed motor. Three leyden-jars of about two gallon capacity were used on each side of the static machine. The spark-gap, O, under investigation was located in a long, collapsible, light-tight wooden box, one end of which contained the illuminating gap, I, and the other the plate-holder, P. The overall length of the box was about 3 metres and the middle section measured 40×40 cm. in cross-section. It was constructed of inch boards and painted black inside. Numerous tin vanes, V, about 3 cm. wide and 28 cm. long, were provided to eliminate reflexion.

The spark-gaps, O and I, were connected in series with a variable inductance, L, through a reversing switch, M, to

Fig. 2.



the terminals, T, of the static machine. A retarding capacity, C, was connected in multiple with the illuminating gap, I. A temporary micrometer gap, S, in multiple with the object gap, O, was located outside of the dark-box. The system was earthed as shown in the figure.

Fig. 2 shows a sectional view of the illuminating gap, I. In this figure, D is a cadmium cylinder, into one end of which is wedged a short piece of #24 magnesium wire, the latter forming one of the terminals of the illuminating gap, I. The cadmium cylinder is in turn fastened to the end of a hard rubber rod, R. The rod, R, slides snugly in a 2·5 cm. glass tube, G, which is held in the wall, B, of the dark-box by means of a cork support, K. The gap distance of I is

adjusted from the plate end of the dark-box by means of a long lever, H, shown in fig. 1.

The capacity of the leyden-jars used in this work was found to be approximately 1430 e.s.u. The inductance consisted of a helix of 25 turns of #00 copper wire wound on a framework 25 cm. in diameter and 35 cm. in length ; its resistance was 0·0131 ohm and its self-inductance measured approximately 340·5 microhenrys.

The theory of this method, which is sometimes called the point-source shadow method, is based on the phenomenon of refraction. The light from a point-source is allowed to fall directly upon a photographic dry plate several metres distant from the source. About half-way between the illuminating source and the plate-holder is placed an object consisting of a fluid stream or an electric discharge. The object differing in density from the air about it causes the light from the point-source to be refracted, with the result that a shadow of the refracting object is cast upon the photographic dry plate.

Observations.

The following photographic investigations were made of the electric-spark discharge at O, using the arrangement of apparatus as exhibited in fig. 1 :—

(a) *Variable Capacity.*—With no inductance, L, in the circuit and with the side-gap, S, eliminated, the effect of varying the retarding capacity, C, was investigated. The latter was varied two leyden-jars at one time, going from one to fifteen jars inclusive for all values of the gap-distance, I. Whenever good shadows appeared on the ground-glass at P, a dozen plates were exposed for a single adjustment of the apparatus. With this disposition of apparatus, it was found that for low values of C a shadow showing the spark in its streamer or brush stage was obtained, while for high values of C the later stages of the spark appeared.

(b) *Variable Inductance.*—The second part of this investi gation involved the introduction of inductance, L, into the circuit as shown in fig. 1. The inductance was varied five turns at one time for constant values of retarding capacity, C. Hence a considerable number of adjustments were necessary to adequately cover this field. The inductance was inserted between the static machine terminal, T, and the retarding capacity, C, as shown in fig. 1. Here it was found that for relatively low values of inductance a

large part of the life-history of the spark could be satisfactorily obtained. The capacity, C, was varied four leyden-jars at one time through a range of one to thirteen jars inclusive, and for any one value of C the inductance, L, was varied throughout its entire range, five turns, or about 70 microhenrys, at one time.

(c) *Parallel Gap.*—Since some of the shadowgraphs representing the spark in its infancy showed streamer effects resembling a heavy brush discharge, it occurred to the writer that, by arranging a temporary micrometer gap outside the dark-box, as shown in fig. 1, extremely early sparking conditions might be photographed, from the faintest spark discharge to probably a very late stage. This supposition was not unfounded, as the plates of this paper will show. In this particular phase of the study the retarding capacity, C, was again varied from one to thirteen leyden-jars, four at one time. Furthermore, various types of object-gaps were constructed and used in this particular phase of the work. The gaps were: (i.) point to point; (ii.) point to vertical wire, #30; (iii.) point to disk; (iv.) disk to vertical wire, #30; and (v.) blade to blade.

(d) *Air-Draft.*—Having read with interest the work done by Hemsalech [8] on an electric spark taking place between two electrodes inclined one to the other while a strong air-blast was directed into the gap-space, it was thought that instantaneous shadowgraphs of a similar arrangement might disclose some new results. The air-pressure was varied from four to ten pounds per square inch in steps of two pounds at one time. The orifice of the air-tube projecting through the base of the object-gap, O, had an inside diameter of 8 mm., and extended to within 5 cm. of the gap-space. The air-draft yielded the best results when used in connexion with the parallel gap, S.

Discussion of Results.

Of the 1264 photographic dry plates exposed to the spark discharge during this investigation, 886 have been catalogued. Four prints of the latter appear herewith showing various possible stages of exceeding interest through which a spark discharge may pass. However, it is not to be supposed that any one spark will necessarily pass through all these stages. Based upon Professor Foley's [9] figures for velocities of sound near its source, the exposures of these prints have been calculated to approximate 3 microseconds.

Fig. 3 (Pl. XVI.) represents a brush discharge of a weak spark. Apparently the energy of the spark has been spent. The configuration near the negative terminal most probably represents diffusion of hot air through which the discharge previously took place. A brush and a glow discharge persist at the positive terminal.

Fig. 4 (Pl. XVI.) represents the "pilot" spark of Trowbridge [10]. According to Schuster and Hemsalech [11], the air lines are now being replaced by metallic lines, the vapour of which is beginning to diffuse into the gap-space.

Fig. 5 (Pl. XVII.) may represent the breaking-up of Trowbridge's [12] "charred hole," or, perhaps, the projection of globules or molecular aggregations [13] from the electrodes into the gap-space.

Fig. 6 (Pl. XVII.) represents the striation stage of the spark discharge. Paalzow [14] discovered that when an electric discharge took place under reduced pressure, striations would result for critical values of resistance. A lantern-slide of this print shows the striations most beautifully.

Summary.

1. Optimum conditions for studies of the early stage of the spark discharge and also of sound-pulses were discovered, the former by the use of an auxiliary gap, the latter by the use of a low variable inductance.

2. The findings of Trowbridge [15] and of Schuster and Hemsalech [16] as to the diffusion of metallic vapour into the gap-space are verified by instantaneous photography.

3. Photographic life-histories of various spark discharges have been obtained, parts of which are reproduced herein.

4. A new method for determining the lag of a needle-gap, for the study of steep wave-front impulses, for the study of vortex rings and explosions is herewith suggested.

This investigation was carried out in the physical laboratory of Indiana University under the direction of Prof. A. L. Foley, to whom the author wishes to express his gratitude for the aid extended and for the facilities placed at his disposal.

References.

(1) 'The Scientific Writings of Joseph Henry,' i. p. 201 (Washington, D.C.).
(2) Fedderson, Pogg. *Ann.* ciii. p. 69 (1859); cxiii. p. 437 (1861); cxvi. p. 132 (1862).
(3) Boys, Proc. Phys. Soc. Lond. xi. p. 1 (1890).
(4) Toepler, Pogg. *Ann.* cxxxi. p. 33 (1867); cxxxiv. p. 194 (1868).
(5) Mach, *Sitz. d. Wien. Akad.* xcviii. p. 1333 (1889).

(6) Wood, Phil. Mag. xlviii. p. 218 (1899); l. p. 148 (1900).
(7) Foley & Sounder, Phys. Rev. xxxv. p. 374 (1912).
(8) Hemsalech, *Comptes Rendus*, cxxx. p. 898 (1900); cxxxii. p. 917 (1901); cxl. p. 1105 (1905); *Journ. de Phys.* l. p. 76 (1902).
(9) Foley, Phys. Rev. xvi. p. 449 (1920).
(10) Trowbridge, Phil. Mag. xxxvi. p. 343 (1893).
(11) Schuster & Hemsalech, Phil. Trans. cxciii. p. 189 (1899); Proc. Roy. Soc. Lond. lxiv. p. 331 (1899).
(12) Trowbridge, *loc. cit.*
(13) *Vide* Author's discussion on the "Mechanism of the Condensed Spark Discharge," Proc. Indiana Acad. of Sci. 1927.
(14) Paalzow, Pogg. *Ann.* cxii. p. 567 (1860); cxviii. p. 178 (1863).
(15) Trowbridge, *loc. cit.*
(16) Schuster & Hemsalech, *loc. cit.*

CXIII. *On the Presence of Charges at an Electrode Surface.*

By William Clarkson, *Ph.D., M.Sc., A.Inst.P., International Education Board Fellow, Physical Institute of the University of Utrecht* *.

I. Introduction.

THE paper describes experiments made to determine whether at any time after an electrical discharge

(1) an electrode gives up a charge;
(2) there is an electric field within some distance of the surface.

They form part of a series of experiments on electrode surface effects as demonstrated by "build-up" lag variations, contact potential variations, and variations of the sparking potential. These effects are invariably present in discharge systems, and are of great significance in their study.

The particular phenomena being heterogeneous, many explanations have been advanced. The changes selected for investigation here may be shown to occur under pure as well as impure conditions, to be reversible and to decay with time. They are ascribable to temporary unstable modifications of the gas-electrode interface; this suggests a change in the work of extraction of an electron.

The most generally applicable hypothesis will be shown to be that of double layers—a potential introduced at the electrode surface; but other explanations deserve consideration. As direct experiments on residual charges might be expected to throw light on this problem, even negative results being of significance, the following experiments were made.

* Communicated by Professor Ornstein.

II. Preliminary Experiments.

1. *General Methods.*

The following description of experiments made to determine whether a charge is given up by an electrode shows the development of the problem.

Condenser discharges in discharge-tubes of great purity[1], and later unidirectional sparks in air, were employed. The effects of merely applying a field were also studied.

The general experimental scheme was as follows: one electrode, X, was connected to a charge-measuring device; this system could be (*a*) earthed or (*b*) insulated. The other electrode, Y, could be (*a*) connected to a suitable source of potential, or (*b*) earthed, in conjunction with this source. A switch permitted the rapid performance of the following sequence of operations: (*a*) X to earth, Y to voltage supply, *i.e.* a discharge, (*b*) Y and potential source earthed, *i.e.* entire system at earth potential, and (*c*) X released. If X now acquired a charge, this must have been derived from some part of a metal system initially at the one potential.

The whole system was screened as completely as possible from all additional influences likely to cause deflexions.

An electroscope proving unsuitable a string-electrometer was employed. It exhibited no appreciable leak and had a limit of sensitivity consistent with stability of 1/100 volt. It capacity was some cms.

2. *Discharge-tubes.*

In the case of discharge-tubes the electrometer showed a deflexion when insulated any time within a minute or two of a discharge. It was equivalent to several volts when the time-interval was of the order of 1/5 sec., and decreased as the time-interval was increased. The sign of the charge was opposite to that of the electrode, and was determined by the direction of the last discharge preceding observation.

It was found, however, that these effects were not due to the electrodes themselves, but to the leakage of charge from the insulating walls of glass; any electrode effects were completely masked. (See Section IV.)

The alternative was to discard discharge-tubes in favour of a spark system in air, as this permitted the problem of insulators to be attacked, but in so doing the advantage of working under pure conditions was lost.

3. *Spark-Gaps.*

Work on spark-gaps with a wide variety of arrangements merely showed that all observable effects could still be

attributed to charges induced on the insulators ; radiations from the discharge were particularly troublesome.

These effects being eliminated, no residual charges could be detected.

4. *Improvements.*

These were directed to the following ends: (1) to attain maximum sensitivity—this meant minimising the capacity : (2) to screen all insulators completely ; and (3) to minimise the time-interval between the discharge and release.

(1) Instead of small pieces of metal, the mounts of the electrometer wire were made of a minimum length of fine wire mounted in glass. The lead was reduced to 3 cm. of 1/10th-mm. wire. All contacts were soldered.

It was necessary to keep the electrometer system easily accessible so that frequent calibration was possible.

(2) With small light electrodes the insulator was correspondingly small ; screening was thus greatly facilitated.

(3) The cycle of operations was made automatic. It was necessary to avoid the transmission of vibrations to the electrometer, these tending to cause a shift in zero.

III. Final Methods.

1. *Charge given up by an Electrode.*

By effecting the refinements suggested, the time-interval between discharge and release was reduced to 1/1000 sec. without loss of sensitivity.

A. *Apparatus.*—The electrode was a fine needle mounted in well-screened amber. Hinged, interlocking jaws of brass gave perfect earthing and completed the screening of the insulator. The needle-point was situated within a thick brass screen at the other side of which was the second electrode. A brass slide could be drawn before the hole, *i. e.* between the electrodes, to complete the earthed screening. A projecting lug was so attached to this that on the hole being covered the jaws were wedged open just sufficiently to release the needle.

The slide was attached to a sliding contact actuated by a falling weight. The impact of the weight occasioned the following sequence of events : (*a*) the contact was made for a short time ; (*b*) it was then broken and the slide drawn, the needle now being quite isolated ; and (*c*) the needle was released.

B. *Observations.*—With the time-interval small appreciable deflexions—up to 1/20 volt—were generally observed. They were very erratic in value and were always negative.

They were not due to vibrations or insulation, and were not associated with the discharge, as they occurred in its absence with an average value the same as that when the needle was anode or cathode. Further, sensitizing [2] or fouling the needle was without influence.

Previous experience suggested the cause, the release of the needle by the jaws. With needle and jaws freshly cleaned the effects were negligible.

The results of the experiment thus were entirely negative.

2. *Field near Electrode Surface.*

A. *Method.*—A circular disk electrode rotating at high speed was employed. The discharge passed at a point on the edge, and a collecting needle was placed as near as was practicable to the opposite end on the diameter. With the needle at the potential of the electrode the presence of a field—presumably attendant on a surface-charge—would be detected by a charging-up of the needle, *i. e.* the electrometer string. Rotation would provide for maintenance of the field.

B. *Apparatus.*—The electrode consisted of a knife-edge ridge round the middle of a light, hollow, brass cylinder, $3 \times 2\frac{1}{2}$ cm. This revolved axially, without vibration, in a metal frame. The side of the drum nearest the discharge was earthed along its whole length by stranded brushes, and the spindle and frame were also earthed. The whole system was then connected to the electrometer case. The drum also served as an earthed screen between the discharge and the collecting point.

The air-gap between the needle and the electrode was 1/10 mm. Tests under working conditions showed that the needle rapidly acquired the potential of the revolving drum.

Speeds up to 200 revs. per second were attainable, *i. e.* 1/400 sec. between discharge and needle; since the discharge was drawn out by the rotation, this figure may be reduced to 1/600 sec.

A continuous discharge not being attainable, a transformer fed by an alternative source of 520 periods per second was used; the discharge lasted throughout most of each period. Generally, unidirectional sparks some 4 mm. long were employed. The electrodes were made symmetrical.

C. *Observations.*—It was found that inconstant deflexions of about 1 volt, positive or negative, were obtained, the positive being about 10 per cent. the greater. The sign was opposite to that of the rotating electrode.

Apart from the effects sought for, these possibly could be

due to two other causes : (1) imperfect earthing of the drum, (2) charged gas being carried round from the discharge. They could not be traced to insulators.

It was sought to remove (2) : firstly, by blowing a jet of air across the electrode between the discharge and the collecting needle, and, secondly, by inserting metal or other screens between them. On this being done, it was found that (*a*) the positive and negative deflexions were now equal at about the mean of their former values ; (*b*) they were independent of whether the screening was a strong or weak current of air, a metal plate or a pad of felt bearing on the electrodes ; and (*c*) they occurred independently of the kind of spark or whether it passed at the middle or the edge of the drum, but increased with the discharge intensity and when the drum contacts became worse. Impurities had no effect.

From this it was concluded that the deflexions were certainly not due to a residual charge on the electrodes, but were attributable to a fall of potential in the drum contacts. The former negative results were thus fully confirmed.

IV. Experimental Conclusions.

The results of the foregoing series of experiments may be summarized as follows : with (*a*) a detecting system of some few cms. capacity and a sensitivity of 1/100 volt; (*b*) discharges in air from brush-discharges to sparks of several mm. or alternating fields ; and (*c*) electrodes, polished or rough, sensitized, clean or impure, it is found that

1. No detectable charge is given up by a steel needle after a 1/1000-sec. interval ; and

2. No field can be detected by a point 1/10 mm. distant from a sharp brass edge after a 1/600-sec. interval.

These results show that there is no appreciable free charge persisting at an electrode surface for a longer period after a discharge than that stated.

Charges amounting to several volts, even with large electrodes, were recovered, however, when the insulator was exposed to the slightest influence of varying fields or of radiations from the discharge. The effect depended on the time-interval, but might last for minutes. Breaking contact might also give rise to a charge.

Results neglecting these possibilities must be received with caution as, in general, the effects are identical with those sought for. In discharge-tubes the effects are great and inevitably present, but it has yet to be shown that they need necessarily help to determine the conditions of discharge.

Discussion.

A general idea of the phenomena of temporary polarization may be derived from a study of preceding work. Further, the results will be applicable to the present case, even though, as just stated, some experiments are open to criticism.

Contact-potential measurements show that polarizations of several volts are detectable in an X-ray discharge-tube several seconds after the cessation of a discharge, or even an applied field [3]. Spark-gaps exhibit similar phenomena [4]. It is stated that a residual charge corresponding to a large fraction of the quantity transferred by the discharge is recoverable [4].

Sparking-potential measurements show that effects of similar magnitude are observable even in pure discharge-tubes [5, 1]; in spark-gaps [6, 10] and α-particle counters [7, 10] they are many times greater.

A lag of several per cent. of the applied voltage (400) with a life of at least 1/50 second has been recorded for the mass-spectrograph [8].

Without claiming any relation between these effects, or proving that they are due to surface-charges, it may certainly be stated that if in any way charges were involved, they could not have failed to be detected in the present experiments, save on one condition *that, with respect to electrical charges, the system responsible for polarization, whether reversible or irreversible, must be a closed one.*

By assuming that reversible polarization is due to a *charged layer at the cathode surface*, however, we are provided with an explanation not only of contact-potential variations [4], but of sparking-potential variations [5], build-up lag variations [1], and the effect of radiations on these [5, 1], for all these may be correlated with variation of the emissivity of the cathode surface.

Grease layers [3], layers of oxide [7] or chemical compounds [2, 8], thick [10] or monomolecular [4, 5] layers of condensed gas, whether native or an impurity, may all be postulated for particular cases. Temporary, reversible, polarization, however, would appear to be a general property of all discharge-systems irrespective of conditions; and if, as has been shown, a closed system of charged layers must be postulated, we must conclude that *reversible polarization is a manifestation of "double-layers" at the cathode surface.* The phenomena mentioned in the preceding paragraph will be but other manifestations of the same influence.

Such layers, whatever the actual mechanism involved, represent dynamic equilibrium of the gas and electrode at

their interface. They will be influenced by electric fields, radiations, and particularly by such an active process as a discharge, where radiations are intense and the gas is abnormally active. On the active agent being removed or reduced, they will be left in unstable equilibrium ; their recovery could conceivably be slow enough to account for the facts cited above.

Summary.

The possibilities of a charge or field existing at an electrode surface after a discharge are investigated.

It is shown that with brass in air no field greater than 1/100 volt was present 1/10 mm. distant after a spark, and no charge as great as 1/100 volt for a capacity of some cms. was given up by a steel needle after 1/1000 second. Impurities etc. caused no appreciable change.

A *résumé* is given of related work, and it shows that if charges actually are involved they must be immeasurably greater than those detectable here. From this it is concluded that, with respect to electrical charges, the system responsible for polarization, whether reversible or irreversible, must be a closed one.

When this conclusion is applied to the charged cathodic layers which are shown to correlate and explain contact potential, sparking potential, and lag variations, it follows that reversible polarization, like them, is a manifestation of " double-layers " at the cathode surface.

Such layers may be expected to attend dynamic equilibrium of the gas-electrode interface.

" Wall " and insulator effects are discussed.

The writer has pleasure in expressing his great obligation to Professor Ornstein and to the International Education Board.

References.

(1) Clarkson, Phil. Mag. iv. p. 121 (1927).
(2) Kovarik, Phys. Rev. xiii. p. 272 (1919).
(3) Compton and Ross (also Ratner etc.), Phys. Rev. iii. p. 207 (1915).
(4) Gaede, etc., etc., *Ann. d. Phys.* xiv. p. 669 (1904).
(5) Taylor, Utrecht Dissertation, Sept. 1928.
(6) Peek (also Züber etc.), ' Dielectric Phenomena,' New York, 1915.
(7) Gorton and Warburg (also Geiger etc.), *Ann. d. Phys.* xviii. p. 28 (1905).
(8) Aston, Proc. Roy. Soc. A, cxv. p. 487 (1926).
(9) See discussion, Proc. Phys. Soc. i. p. 13 (1926).
(10) Zelany, Phys. Rev. xvi. p. 102 (1920); xix. p. 556 (1922).

CXIV. *On the Fine Structure of the Spectrum Lines of Thallium in the Ultra-violet.*

By Wali Mohammad, *M.A. (Punjab), B.A. (Cantab.), Ph.D. (Göttingen), Professor of Physics, Lucknow University, and* S. B. L. Mathur, *M.Sc.* *

I. *Introduction.*

THE work under report forms the third instalment of the investigation undertaken by the authors on the fine structure of the spectrum lines in the ultra-violet. The authors' results on cadmium have been published in the Phil. Mag. of July, 1927 while those on zinc are under publication.

II. *Previous Work.*

Some of the thallium lines appear to have been among the first to be investigated for fine structure.

Michelson [1], Fabry and Perot [2], and Janicki [3] determined the structure of λ 5351, while Barnes [4] investigated λ 5439. Back [5], in course of his researches on the Zeeman effect of certain lines, has dealt with the structure of the lines λ 5351, λ 3776, and λ 2767. These appear to be the only four lines of thallium of which the fine structure has been attempted.

III. *Experimental Arrangement.*

The experimental arrangement was the same as described previously. Briefly stated, light from an arc in vacuum consisting of a Wehnelt oxy-cathode of platinum and the anode of thallium was rendered parallel by means of a quartz lens, and allowed to fall on a Hilger Quartz Lummer-Gehrcke plate (13 cm. long, 0·46 mm. thick). The interference fringes from the upper face of the L.-G. plate were focussed on the slit of a Hilger E_3 quartz spectrograph and photographed on Ilford Special Rapid plates. The wavelength of the satellites was calculated from von Baeyer's formula. As a control the cadmium line λ 4800, which has been examined by several investigators, was photographed and its structure determined. The agreement between the observed values of other experimenters and our own was sufficiently close to show that the Lummer plate was giving satisfactory results.

* Communicated by the Authors.

IV. *Difficulties.*

Among the difficulties met with in working out the photographs, the following are worth mentioning :—

(*a*) Absence of a means of eliminating a ghost if one is present. The performance of the given plate showed it to be almost free from ghosts, but another plate or, still better, a crossed plate arrangement would have been more desirable.

(*b*) The fringes are not always sharp—some components are well defined, while others are somewhat diffuse. This makes accurate measurement difficult.

V. *Results.*

The results of the investigation are given below. The wave-lengths are taken from Exner and Haschek, and the figures in brackets indicate the intensity as estimated from the photographs.

(1) *Line* 3775·89 (500).

This line shows six satellites as follows :—

+0·054 (5), +0·042 (5), +0·017 (9), 0·000 (10),
−0·020 (9), −0·035 (6), −0·052 (5).

It will be noted that the satellites are situated more or less symmetrically about the principal line.

This is an interesting line, as the recent experiments of Grotrian[6] and Carroll[7] have indicated that the ground orbit of the valence electron is 1, π orbit and not 1, σ orbit as in the case of other metals. Narayan[8] and his co-workers found that the absorption band λ 3775 is distinctly asymmetrical, being sharply defined on the wave-length side, but with increasing density of the vapour gradually spreads out towards the red end. They concluded that this line shows the existence of anomalous dispersion. Back, using a concave grating, found the following structure :—

+0·058 (3), 0·000 (10) double?, −0·101 (8).

It should be noted that Back suspects the principal line itself to be double, but gives no clue to its structure.

(2) *Line* 3529·52 (100).

The line appears to have the following structure :—

0·000 (10), −0·027 (6).

There is some doubt about the sign of this satellite. In some photographs the satellite appears to be negative, while

in others it appears to be positive. In two of the photographs a very faint satellite appears at +0·044, and in four others another satellite at −0·047. Combining all these values, we get the following structure :—

+0·044, 0·000, −0·027, −0·047.

(3) *Line* 3519·38 (500).

This line shows the following structure :—

+0·043 (8), +0·026 (6), 0·000 (10), −0·015 (9), −0·029 (6), −0·044 (6).

(4) and (5) *Lines* 3229·89 (20) and 3230·7 (1).

This is a doublet consisting of two lines of unequal intensity, the one of longer wave-length being very faint indeed. Its close proximity to the line 3229·89 makes it very difficult to differentiate a satellite from the weak principal line. The structure of line 3229·89 is as follows :—

0·000 (10), −0·019 (5).

There is a suspicion of another satellite at −0·038, but it may be due to a ghost.

(6) *Line* 2921·66 (20).

This line shows only one satellite :—

+0·016 (9) ; 0·000 (10).

(7) *Line* 2918·42 (100).

This line also only shows one satellite :—

+0·027 (9) ; 0·000 (10).

Two photographs on two different plates show another satellite situated at −0·019.

(8) *Line* 2826·45 (10).

This line also shows one satellite :—

+0·023 (5) ; 0·000 (10).

(9) *Line* 2767·87 (20).

This line was found by the authors to possess three satellites clustered together about the principal line. But the satellites were not well resolved and could not be measured. Back gives the following structure of this line:—

2767·913 (5),
·882 (4),
·852 (3),
·833 (3).

(10) and (11) *Lines* 2710·74 (5) and 2709·33 (20).

This again, is a close doublet. Both the lines appear to be simple, but, on account of the faintness of the images on the photographs, this cannot be decided with certainty.

(12) *Line* 2580·25 (3).

This line appears simple. As in the former case, on account of the faintness of the image, the conclusion is not definite.

VI. *Summary.*

Thallium is not very rich in lines. According to Exner and Haschek there are 21 lines between 6550·15 and 2580·25. Out of these, 11 are very weak, having an intensity less than 4 (maximum intensity 500) and thus, except 2580·25, these could not be photographed. The structure of the remaining lines has been determined for the first time. Further work on the structure and the energy-levels is in progress.

References.

(1) Michelson, Phil. Mag. (5) xxxiv. pp. 280–299 (1892).
(2) Fabry and Perot, *Comptes Rendus*, cxxvi. pp. 407–410 (1898); also *Ann. de Chim. et Phys.* xvi. pp. 115–144 (1899).
(3) Janicki, *Ann. de Physik*, xix. pp. 36–79 (1906); *ibid.* xxix. pp. 856–857 (1909).
(4) Barnes, Astrophys. Journ. xix. pp. 190–211 (1904); Phil. Mag. (6) vii. pp. 485–503 (1904).
(5) Back, *Ann. de Physik*, lxx. pp. 333–372 (1923).
(6) Grotrian, *Zeits. f. Physik*, vols. ii., iii., & iv. pp. 218–31 (1922).
(7) Carroll, Proc. Roy. Soc. A, vol. ciii. pp. 334–339 (1923).
(8) Narayan, Proc. Roy. Soc. A, cvi. p. 596 (1924).

CXV. *On a Curious Optical Theorem and its Geometrical Basis.* *By* Alfred A. Robb, *Sc.D., F.R.S.**

THE following curious theorem, though purely geometrical in its character, is most simply understood from an optical illustration; and, indeed, it was from this standpoint that the writer originally arrived at the result.

Let us imagine a shell exploding in free space into n particles, which fly off in various directions with various velocities, and suppose that, after the explosion, a flash of light starts out from particle 1 at any instant P and goes to particle 2, thence to particles 3, 4 ... n in succession, and finally back to particle 1, where it arrives at an instant Q.

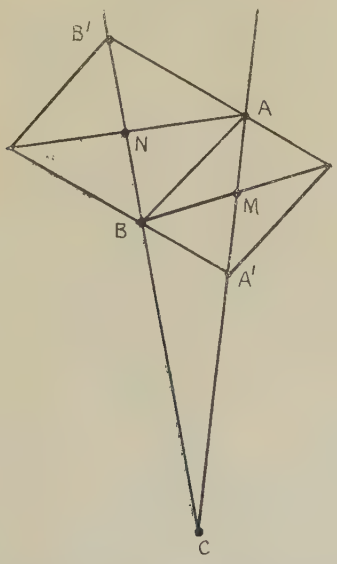
* Communicated by the Author.

Further, suppose a second flash of light starts out from particle 1, also at the instant P, and makes a circuit of the particles in the reverse order ; that is to say, it goes first to particle n, thence to particle $n-1$, and so on in succession back to particle 1 ; then the theorem asserts that it will also arrive at the instant Q.

The assumptions are that the n particles start from simultaneous contact and move with uniform velocities.

The result is very simply deduced on the basis of the author's 'Theory of Time and Space,' but may also be proved in other ways.

Fig. 1.



Let CA and CB be two intersecting inertia lines, and let AB be an optical line intersecting both, so that B is *after* C and A is *after* B.

Let the second optical line through A in the plane of ABC intersect CB in B′, and let the second optical line through B in the plane intersect CA in A′.

If M be the centre of an optical parallelogram of which A′, B, and A are three corners, we know that BM is normal to A′A.

Similarly, if N be the centre of an optical parallelogram of which B, A, and B′ are three corners, we have AN normal to BB′.

Let us denote the lengths: CB by a, CA by b, MA by g, BN by h, and let the hyperbolic angle BCA be denoted by C. Then we have:

$$\frac{a+h}{b} = \cosh \mathrm{C} = \frac{b-g}{a}.$$

Thus

$$h = b \cosh \mathrm{C} - a$$

and

$$g = b - a \cosh \mathrm{C}.$$

Also, since A′B and AB′ are parallel, we have:

$$\frac{2g}{2h} = \frac{b-2g}{a}.$$

Thus

$$\frac{b-a\cosh \mathrm{C}}{b\cosh \mathrm{C}-a} = \frac{2a\cosh \mathrm{C}-b}{a}$$

or

$$a^2+b^2-2ab\cosh \mathrm{C}=0.$$

Thus

$$\cosh \mathrm{C} = \frac{a^2+b^2}{2ab} = \frac{1}{2}\left(\frac{b}{a}+\frac{a}{b}\right).$$

Comparing this with the formula

$$\cosh \mathrm{C} = \tfrac{1}{2}(e^{\mathrm{C}}+e^{-\mathrm{C}}),$$

we find for the absolute value of C,

$$\mathrm{C} = \log \frac{b}{a},$$

since

$$b(b-2g)=a^2,$$

and therefore $b>a$.

Thus, if we have two particles separating from contact, and moving with uniform velocity with respect to one another, and we measure "local times" from the instant of contact; then, if a flash of light starts out from the one at "local time" a, and arrives at the other at "local time" b, we shall have

$$\mathrm{C} = \log \frac{b}{a},$$

where C is what I have elsewhere called the "rapidity" * of the one particle with respect to the other.

* The rapidity is defined thus:

$$\text{rapidity} = \tanh^{-1}\frac{v}{\mathrm{V}},$$

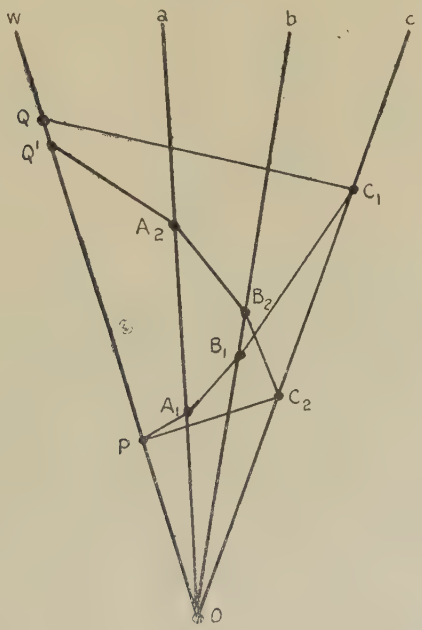
where v is the velocity of the one particle with respect to the other and V is the velocity of light.

In order now to prove the theorem, let Ow, Oa, Ob, Oc, ... be a set of inertia lines all intersecting in O.

For the sake of definiteness suppose that we have just four, though the method of proof obviously applies to any number.

Take any element P in Ow which is *after* O.

Fig. 2.



Let A_1 be the first element in Oa which is *after* P,
„ B_1 „ „ Ob „ „ A_1,
„ C_1 „ „ Oc „ „ B_1,
„ Q „ „ Ow „ „ C_1.

Similarly,

let C_2 be the first element in Oc which is *after* P,
„ B_2 „ „ Ob „ „ C_2,
„ A_2 „ „ Oa „ „ B_2,
„ Q′ „ „ Ow „ „ A_2.

Then PA_1, A_1B_1, B_1C_1, C_1Q are all optical lines.
Similarly PC_2, C_2B_2, B_2A_2, A_2Q' are all optical lines.

Thus, using our formula for the hyperbolic angle, we see that

$$\frac{OA_1}{OP} = \frac{OQ'}{OA_2},$$

$$\frac{OB_1}{OA_1} = \frac{OA_2}{OB_2},$$

$$\frac{OC_1}{OB_1} = \frac{OB_2}{OC_2},$$

$$\frac{OQ}{OC_1} = \frac{OC_2}{OP}.$$

Thus, multiplying corresponding sides, we get

$$\frac{OQ}{OP} = \frac{OQ'}{OP}$$

or $$OQ = OQ',$$

and, since Q and Q′ are each *after* O, it follows that Q′ must be identical with Q, as was to be proved.

A similar result will obviously hold if we suppose that the particles are all approaching simultaneous contact and the flashes of light start out *before* the instant of contact.

Apart from Time-Space theory, the theorem has an interpretation in ordinary three-dimensional geometry and also in Euclidean geometry of any higher number of dimensions. We shall state the theorem as it holds for the case of three dimensions.

Referring to fig. 2, suppose that we have any number n of straight lines all intersecting in a point O, and such that they all lie inside a certain quadric cone having O as vertex.

Now if, for convenience of reference, we call one half of the cone the "upper half" and the other the "lower half," and, taking a point P on the first of the set of straight lines and lying (say) inside the upper half of the cone, let the upper half of a similar and similarly situated cone having P as vertex intersect the second line in a point A_1.

Again, let the upper half of a similar and similarly situated cone having A_1 as vertex intersect the third line in a point B_1.

Proceeding thus round the whole set of straight lines, we arrive at last at a point Q in the first line.

The theorem then asserts that, starting again at P, and making the circuit of the lines in the reverse order, we arrive again at the same point Q.

Any line passing through the origin and whose equations are

$$\frac{x}{l} = \frac{y}{m} = \frac{z}{n},$$

will lie within the cone

$$\frac{z^2}{c^2} - \frac{x^2}{a^2} - \frac{y^2}{b^2} = 0, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

provided that

$$\frac{n^2}{c^2} - \frac{l^2}{a^2} - \frac{m^2}{b^2} > 0. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The cone (1) is asymptotic to the system of hyperboloids of two sheets :

$$\frac{z^2}{c^2} - \frac{x^2}{a^2} - \frac{y^2}{b^2} = \mathrm{K}^2. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

If now we consider the region inside one half of the cone (1), the position of any point in the region may be determined if we know the direction cosines of the radius vector from the origin through the point, together with the value of K for the particular hyperboloid of the system which passes through the point. Thus, if the point lies in the line

$$\frac{x}{l} = \frac{y}{m} = \frac{z}{n} = r,$$

we shall have

$$\left(\frac{n^2}{c^2} - \frac{l^2}{a^2} - \frac{m^2}{b^2}\right) r^2 = \mathrm{K}^2 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

for the point in question.

Consider now any two lines passing through the origin and satisfying condition (2), say

$$\frac{x}{l_1} = \frac{y}{m_1} = \frac{z}{n_1} = r$$

and

$$\frac{x}{l_2} = \frac{y}{m_2} = \frac{z}{n_2} = r,$$

and let (x_1, y_1, z_1, r_1) be any point on the first line which lies within the selected half of the cone (1).

The equation of a cone similar and similarly situated to cone (1), but having its vertex at this point, will be

$$\frac{(z - n_1 r_1)^2}{c^2} - \frac{(x - l_1 r_1)^2}{a^2} - \frac{(y - m_1 r_1)^2}{b^2} = 0. \quad . \quad (5)$$

If this cone intersects the second line in a point (x_2, y_2, z_2, r_2), we shall have

$$\frac{(n_2r_2-n_1r_1)^2}{c^2}-\frac{(l_2r_2-l_1r_1)^2}{a^2}-\frac{(m_2r_2-m_1r_1)^2}{b^2}=0.$$

This may be written in the form

$$\left(\frac{n_2^2}{c^2}-\frac{l_2^2}{a^2}-\frac{m_2^2}{b^2}\right)r_2^2-2\left(\frac{n_2n_1}{c^2}-\frac{l_2l_1}{a^2}-\frac{m_2m_1}{b^2}\right)r_2r_1 + \left(\frac{n_1^2}{c^2}-\frac{l_1^2}{a^2}-\frac{m_1^2}{b^2}\right)r_1^2=0.$$

If now K_1 and K_2 be the values of the Ks for the points (x_1, y_1, z_1, r_1) and (x_2, y_2, z_2, r_2) respectively, this last result may be written in the form

$$K_2^2-2\frac{\left(\frac{n_2n_1}{c^2}-\frac{l_2l_1}{a^2}-\frac{m_2m_1}{b^2}\right)}{\sqrt{\left(\frac{n_2^2}{c^2}-\frac{l_2^2}{a^2}-\frac{m_2^2}{b^2}\right)}\sqrt{\left(\frac{n_1^2}{c^2}-\frac{l_1^2}{a^2}-\frac{m_1^2}{b^2}\right)}}K_2K_1+K_1^2=0.$$

Now it is to be observed that this equation is symmetrical with respect to the two lines (l_1, m_1, n_1) and (l_2, m_2, n_2), so that we can make the substitution $\begin{pmatrix} l_2 m_2 n_2 l_1 m_1 n_1 \\ l_1 m_1 n_1 l_2 m_2 n_2 \end{pmatrix}$ without altering it. Also we can interchange K_2 and K without altering the equation.

It may be proved that, under the conditions

$$\left(\frac{n_1^2}{c^2}-\frac{l_1^2}{a^2}-\frac{m_1^2}{b^2}\right)>0 \quad \text{and} \quad \left(\frac{n_2^2}{c^2}-\frac{l_2^2}{a^2}-\frac{m_2^2}{b^2}\right)>0,$$

the roots of this equation (regarded as an equation for K_2 in terms of K_1) are always real, and only become equal when the lines (l_1, m_1, n_1) and (l_2, m_2, n_2) coincide.

Further, if K_2' and K_2'' be the two roots, we have $K_2'K_2''=K_1^2$, so that one of them (say K_2'') is greater than K_1, while the other (say K_2') is less than K_1.

But we know that a line which is parallel to any line which would lie within a cone will itself intersect the cone in two points, one of which lies on one half of the cone and the other on the other half; so that K_2'' will correspond to a point on one half of cone (5), while K_2' will correspond to a point on the other half.

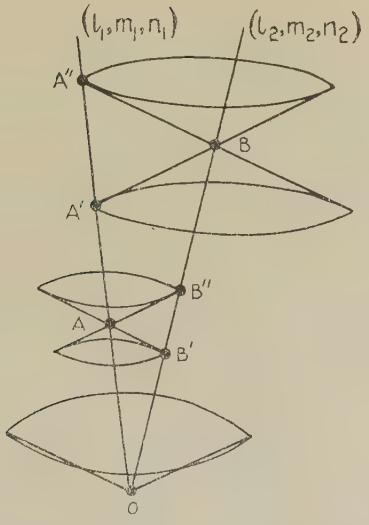
If, then, for convenience of reference, we refer to the halves of these similar and similarly situated cones as "upper" halves and "lower" halves, and suppose that the

point (x_1, y_1, z_1, r_1) lies inside the upper half of cone (1), then it is easy to see that the point corresponding to K_2'' lies on the upper half of cone (5), while the point corresponding to K_2' lies on the lower half of cone (5).

Thus the ratio $\frac{K_2''}{K_1}$ will be the larger root of the equation

$$\left(\frac{K_2}{K_1}\right)^2 - 2\frac{\left(\frac{n_2n_1}{c^2} - \frac{l_2l_1}{a^2} - \frac{m_2m_1}{b_2}\right)}{\sqrt{\frac{n_2^2}{c^2} - \frac{l_2^2}{a^2} - \frac{m_2^2}{b^2}}\sqrt{\left(\frac{n_1^2}{c^2} - \frac{l_1^2}{a^2} - \frac{m_1^2}{b^2}\right)}}\left(\frac{K_2}{K_1}\right) + 1 = 0 \quad . \quad . \quad . \quad (6)$$

Fig. 3.



and this is a perfectly definite number which s independent of the actual position of the point (x_1, y_1, z_1, r_1) on the line (l_1, m_1, n_1).

In the same way, if we take a cone similar and similarly situated to cone (1), and having its vertex inside the selected half of cone (1) on the line (l_2, m_2, n_2), we shall arrive at the same quadratic equation for the ratio of the K of a point of intersection of this cone with the line (l_1, m_1, n_1) to the K of the vertex of the cone.

Also the larger root of the equation will be the ratio of the K of the point of intersection of the line (l_1, m_1, n_1) with the upper half of the cone to the K of the vertex.

Thus, provided we confine ourselves to the upper halves of the cones, we get the same ratio for the K of the point of intersection to the K of the vertex, no matter which of the two lines the vertex lies in, and no matter where it lies in either line. Thus, if we denote the K coordinate of a point A by K(A), our results, as illustrated in the figure, are as follows :—

$$\frac{K(B'')}{K(A)} = \frac{K(A'')}{K(B)},$$

no matter where A may be situated on the line (l_1, m_1, n_1) or where B may be situated on the line (l_2, m_2, n_2), provided that A and B lie inside the upper half of the cone whose vertex is O.

Also

$$\frac{K(B')}{K(A)} = \frac{K(A')}{K(B)}.$$

Further,

$$K(B') \,.\, K(B'') = \{K(A)\}^2$$

and

$$K(A') \,.\, K(A'') = \{K(B)\}^2.$$

Similar results hold, of course, if A and B lie inside the lower half of the cone whose vertex is O.

Making use of these K coordinates, we are now in a position to prove the theorem in a manner exactly analogous to that in which we proved it for the Time-Space case.

Thus, referring again to fig. 2, we have

$$\frac{K(A_1)}{K(P)} = \frac{K(Q')}{K(A_2)},$$

$$\frac{K(B_1)}{K(A_1)} = \frac{K(A_2)}{K(B_2)},$$

$$\frac{K(C_1)}{K(B_1)} = \frac{K(B_2)}{K(C_2)},$$

$$\frac{K(Q)}{K(C_1)} = \frac{K(C_2)}{K(P)}.$$

Thus, multiplying corresponding sides, we get

$$\frac{K(Q)}{K(P)} = \frac{K(Q')}{K(P)}$$

or

$$K(Q) = K(Q'),$$

and therefore Q′ and Q lie on the same hyperboloid and on the same sheet of it.

But Q′ and Q also lie on the same line through the origin, and so it follows that Q′ must be identical with Q, as was to be proved.

It is clear that a similar result holds if, instead of taking the points of intersection of the various lines with the upper halves of the cones, we always take the points of intersection with the lower halves.

In considering the extension of this theorem to space of more than three dimensions, there are several points which have to be observed.

In the first place the equation of any proper cone in three dimensions may always be put in the form

$$\frac{x^2}{a^2}+\frac{y^2}{b^2}-\frac{z^2}{c^2}=0.$$

If we make a second square negative, we get a cone of the same general type. If, on the other hand, we consider cones in more than three dimensions, things are rather more complicated.

Thus in four dimensions we should have two essentially different types of cone whose equations might be put in one of the forms

$$\frac{x^2}{a^2}+\frac{y^2}{b^2}+\frac{z^2}{c^2}-\frac{w^2}{d^2}=0,$$

and

$$\frac{x^2}{a^2}+\frac{y^2}{b^2}-\frac{z^2}{c^2}-\frac{w^2}{d^2}=0.$$

Only the first of these can be divided into two halves by a single point, and this is the type of cone to which the theorem directly applies.

In general, for a larger number of dimensions than three, say for m, the equation of the cone, when expressed as the sum of m squares equated to zero, must be such that all the squares *with one exception* are of the same sign.

Under these circumstances it may be proved that the roots of the quadratic equation for K_2 in terms of K_1 are always real under conditions analogous to those which we gave when considering the three-dimensional case.

There is a limiting case of this theorem in which the n straight lines are all parallel instead of meeting in a point, but are such that any one of them would lie within a quadric cone of given form and orientation, having its vertex on the line. It may hardly be regarded as necessary to give

a separate proof of this, since we have proved that it must hold for the case of lines all passing through one point, however distant the point may be and however small the angles between them. As, however, the actual method of proof breaks down for the case of parallel lines, the following hints as to the mode of procedure may prove useful.

Let the system of lines be

$$\frac{x-\bar{x}}{l}=\frac{y-\bar{y}}{m}=\frac{z-\bar{z}}{n}=r,$$

where $$\frac{n^2}{c^2}-\frac{l^2}{a^2}-\frac{m^2}{b^2}>0 \quad \text{as before,}$$

and, for convenience, let the points $(\bar{x}, \bar{y}, \bar{z})$ be always selected, so that

$$\frac{l\bar{x}}{a^2}+\frac{m\bar{y}}{b^2}-\frac{n\bar{z}}{c^2}=0,$$

which is always possible provided that

$$\frac{l^2}{a^2}+\frac{m^2}{b^2}-\frac{n^2}{c^2}$$

be not zero, as is here the case.

Proceeding as before, we find that

$$\left(\frac{n^2}{c^2}-\frac{l^2}{a^2}-\frac{m^2}{b^2}\right)(r_2-r_1)^2=\left\{\frac{(\bar{x}_2-\bar{x}_1)^2}{a^2}+\frac{(\bar{y}_2-y_1)^2}{b^2}-\frac{(\bar{z}_2-\bar{z}_1)^2}{c^2}\right\}.$$

It may be proved that the expression on the right can never be negative, provided that

$$\frac{l^2}{a^2}+\frac{m^2}{b^2}-\frac{n^2}{c^2}<0$$

and

$$\frac{l(\bar{x}_2-\bar{x}_1)}{a^2}+\frac{m(\bar{y}_2-\bar{y}_1)}{b^2}-\frac{n(\bar{z}_2-\bar{z}_1)}{c^2}=0,$$

(as is here the case), and it can only be zero when

$$\bar{x}_2-\bar{x}_1=\bar{y}_2-\bar{y}_1=\bar{z}_2-\bar{z}_1=0\ ^*.$$

Since the above equation for (r_2-r_1) is unaltered when we make the substitution

$$\begin{pmatrix}\bar{x}_2\,\bar{y}_2\,\bar{z}_2\,\bar{x}_1\,\bar{y}_1\,\bar{z}_1\\ \bar{x}_1\,\bar{y}_1\,\bar{z}_1\,\bar{x}_2\,\bar{y}_2\,\bar{z}_2\end{pmatrix},$$

we may prove our theorem in a manner analogous to that

* A similar result holds for n dimensions.

previously employed, except that we use differences instead of ratios, and add instead of multiply.

In the optical problem the analogous state of things would be that in which the n particles remained at constant distances from one another, and one would hardly be surprised, in this case, that the light should take the same time to make the circuit in one order as it does in the reverse order.

CXVI. *An Optical Method of Measuring Small Vibrations.*

By H. A. Thomas, *M.Sc., and* G. W. Warren, *B.Sc. (of the National Physical Laboratory)* *.

Summary.

An interferometer method of measuring small mechanical vibrations, such as those encountered in telephone diaphragms and structures, is described, and its application to the measurement of the vibration of a stiff reed is considered. Substantial agreement between the theory of such a vibration is obtained, and its use for the study of the vibration of light moving systems is suggested.

Description of Method.

The essential principle of operation is that of an interferometer in which one plate is attached to the vibrating system and the other plate is fixed. Referring to fig. 1(A), a small glass plate 0·5 cm. square and 1 mm. thick optically plane was ground on one side so as to be non-reflecting. This block A was gummed to a vibrating reed B, actuated by the magnet mechanism C. This reed and magnet was a standard cone loud speaker movement.

Above this block a second sheet of glass D was supported by the brass carriage E, which was capable of adjustment by means of three screws F. These screws served to adjust the plate D until it was parallel to A, and were tapped into a rigid block G fixed to the stationary portion of the magnet mechanism.

A quartz mercury vapour lamp H and lens J gave a parallel beam, and a monochromatic filter K permits only the mercury green ray of wave-length $0{\cdot}5461 \times 10^{-3}$ mm. to be admitted to the interferometer. The glass prism L gave

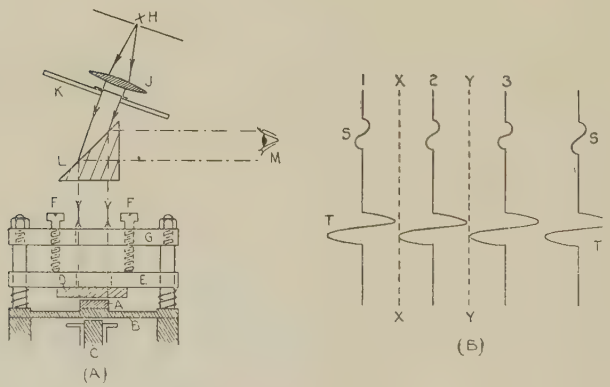
* Communicated by Sir J. E. Petavel, K.B.E., F.R.S.

a reflexion of the reflected beam from A, which can, therefore, be observed by the eye at M.

With the block A stationary, interference fringes are observed at M, as shown in fig. 1 (B), and if the block A moves $\frac{\lambda}{2}$, where λ is the wave-length of the light, the fringes will shift once, *i. e.*, fringe 1 will shift to position 2, 2 will shift to position 3, and so on.

Now let the reed vibrate a very small amount, and assume that its vibrations are sinusoidal in form, then all the fringes will execute a simple harmonic motion about the original stationary position and always parallel to that position.

Fig. 1.



This is illustrated at S, and it is clear that the fringes will disappear, but if the amplitude is now increased till the peak value of the reed movement is $\frac{\lambda}{4}$, we shall get a peak movement of each fringe equal to half the distance between successive fringes, as shown at T, and since the fringes 1 and 2 remain longest along the line X, a fringe will appear due to the persistence of vision. Similarly a fringe Y will appear, and therefore when the amplitude of vibration reaches a maximum value of $\frac{\lambda}{4}$, a new set of fringes will appear equally spaced as before, but shifted by half the distance between a pair of the original fringes.

If the amplitude is still further increased, the fringes will

again disappear and will reappear when the maximum amplitude is $\frac{\lambda}{2}$, and so on. In this way we see that we get no fringes at maximum amplitudes of $\frac{\lambda}{8}$, $\frac{3\lambda}{8}$, $\frac{5\lambda}{8}$, $\frac{7\lambda}{8}$, etc., or in general $\frac{\lambda}{8}+\frac{n\lambda}{4}$ where "n" is an integer, and fringes at amplitudes of $\frac{\lambda}{4}$, $\frac{2\lambda}{4}$, $\frac{3\lambda}{4}$, etc., or in general $\frac{n\lambda}{4}$.

Since the rapidity of movement is greatest for a large amplitude, the visibility of the fringes gets poorer as "n" is increased, but it was found possible to count the reappearances up to 30 shifts. The point of disappearance was more definite than the point of maximum fringe intensity, and the accuracy with which this disappearance could be detected was found to be 1 per cent. of one wave-length of the light used. This corresponds to 1 per cent. of $0{\cdot}5\times10^{-4}$ cm. $=$ $0{\cdot}5\times10^{-6}$ cm.

Application to the Study of a Vibrating Reed.

The loud speaker reed used for the preceding vibrating object was examined at various audible frequencies and amplitudes.

The relation between movement and current at various frequencies is shown in fig. 2, from which it will be noticed that the amplitude is very nearly proportional to the current. Plotting amplitude against frequency for two values of current, viz., 1 milliampere and 0·5 milliampere, we obtain fig. 3, which shows the resonance of the reed at a frequency of 1060.

It is interesting to compare the shape of this response characteristic with constant input current with the theory of a vibrating reed with fixed supports at both ends.

The general law of motion for a reed with a forcing vibration of sinusoidal form can be expressed as

$$\ddot{x}+b\dot{x}+\frac{\mu}{m}x=\frac{\mathrm{F}}{m}\cos\omega t,$$

where
$\omega = 2\pi\times$ frequency,
F = Maximum value of the applied force,
m = Mass of moving body,
μ = an elastic constant,
b = a damping constant.

Fig. 2.

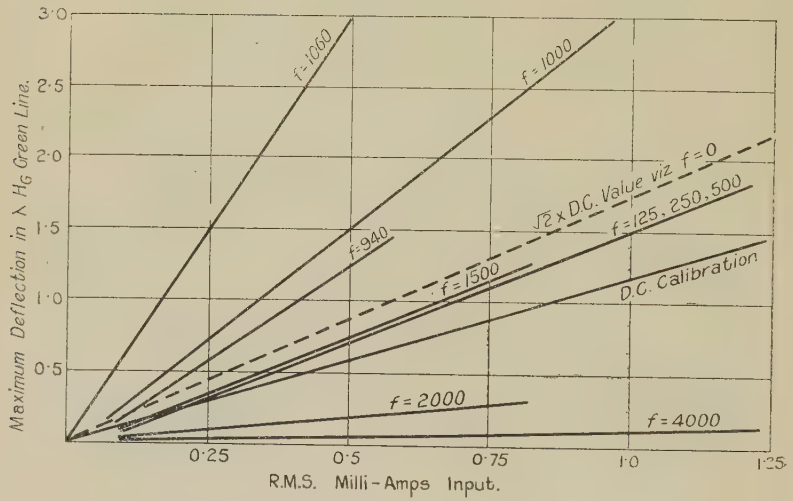
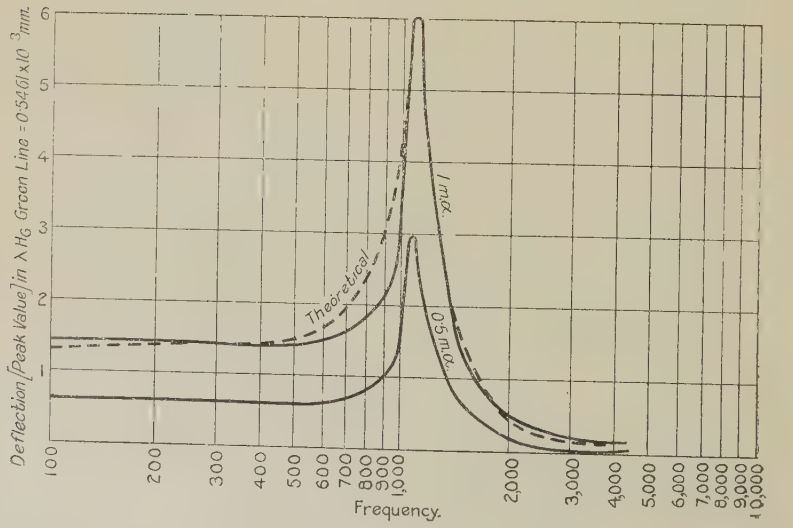

Maximum Deflection in λ H_G Green Line.
3·0
2·5
2·0
1·5
1·0
0·5
f=1060
f=1000
f=940
f=1500
√2 x D.C. Value viz f=0
f=125, 250, 500
D.C. Calibration
f=2000
f=4000
0·25
0·5
0·75
1·0
1·25
R.M.S. Milli-Amps Input.

Fig. 3.


Deflection [Peak Value] in λ H_G Green Line = 0·5461 x 10⁻³ mm.
6
5
4
3
2
1
1 max.
0·5 max.
Theoretical
100
200
300
400
500
600
700
800
900
1,000
2,000
3,000
4,000
5,000
6,000
7,000
8,000
9,000
10,000
Frequency.

The particular solution of this differential equation is of the form

$$x = \frac{\mathrm{F}}{m\sqrt{\left(\frac{\mu}{m}-\omega^2\right)^2 + b^2\omega^2}}\cos(\omega t - \phi),$$

where

$$\tan\phi = \frac{b\omega}{\left(\frac{\mu}{m}-\omega^2\right)},$$

and the maximum displacement at a frequency $f = \frac{\omega}{2\pi}$

$$\hat{x} = \frac{\mathrm{F}}{m\sqrt{(\omega_0{}^2-\omega^2)^2 + b^2\omega^2}},$$

where ω_0 is $2\pi \times$ the natural frequency of the reed

$$\omega_0 = \sqrt{\frac{\mu}{m}} \text{ and so at resonance } \hat{x} = \frac{\mathrm{F}}{mb\omega},$$

and at a frequency far removed from resonance

$$\hat{x} = \frac{\mathrm{F}}{m(\omega_0{}^2-\omega^2)}.$$

In general

$$\hat{x} = \frac{\mathrm{A}}{\sqrt{(f_0{}^2-f^2)^2 + \frac{b^2f^2}{4\pi^2}}},$$

where f_0 = the natural frequency of the reed,
f = the applied frequency,
and A is a constant.

Taking the measured value of $\hat{x}$ at resonance in our case and substituting, we get

$$\frac{\mathrm{A}}{b} = \frac{3180}{2\pi},$$

and substituting the measured value of $\hat{x}$ at a frequency of 50 cycles per second obtained by exciting the magnet from a 50 cycle alternator, we get

$$\mathrm{A} = 0{\cdot}672 \times 10^6, \text{ a constant of the reed,}$$
and $$b = 1{\cdot}33 \times 10^3, \text{ the damping constant.}$$

Using these values, we can now calculate the amplitude at any other frequency. This theoretical curve is shown in fig. 3, and comparative agreement with the experimental results is noticed.

The resonance value of the vibration amplitude with an input of 1 milliampere was only $\frac{3}{1000}$ mm. When the reed is loaded by a loud speaker diaphragm, this resonance peak will be seriously reduced and so we see that the movement of a cone type of loud speaker with good signal intensity, corresponding to a current of 1 milliampere, is of the order of $0{\cdot}75 \times 10^{-3}$ mm. at frequencies below the natural resonance of the reed, and above this resonance frequency, the amplitude is of the order of $0{\cdot}1 \times 10^{-3}$ mm. At an amplitude of this value the accuracy of measurement is 5 per cent.

With a movement of 10^{-3} mm. the accuracy is 0·5 per cent., and at the maximum movement which can be measured at present, due to poor visibility at large amplitudes, viz., 4×10^{-3} mm., the accuracy is 0·12 per cent.

The method can readily be adopted to measure small vibrations of light systems, since the necessary reflecting surface attached to the vibrating system can be obtained in various ways which would introduce no appreciable loading effect.

A thin metal film could be sputtered on to the surface, as it is not necessary to have a perfectly flat surface. If the fringes are not straight, the same shifting effect will occur and the accuracy will in no way be affected.

CXVII. *Note on the Construction of a Valve Oscillator for use in Conductivity Measurements.* *By* J. W. Woolcock, *B.A.*, *and* D. M. Murray-Rust, *B.A.**

A valve oscillator similar to that described by Ulich † has been constructed by the authors and applied to the measurement of the conductivity of dilute solutions of acids and salts in non-aqueous solvents. Excellent minima are obtained even with resistances as high as 100,000 ohms, provided that not only the resistances but also the capacities in the bridge circuit are accurately balanced. The purpose of this note is to describe how such an instrument may conveniently be made from components sold in this country for the construction of broadcast receivers. Experiments with other types of valve oscillator gave far less satisfactory

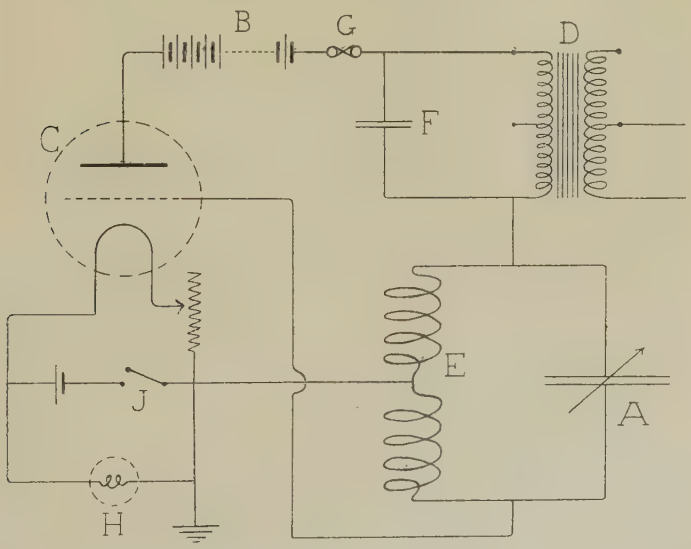
* Communicated by Sir Harold Hartley, F.R.S.

† *Zeits. physikal Chem.* cxv. p. 377 (1925).

results than those obtained with the apparatus described here.

As the diagram shows, the circuit is of the auto-coupled type. The instrument consists of the oscillator unit, the variable condenser A, the dry cells B supplying the high tension, and a 2-volt accumulator to supply the filament current, the whole being enclosed in a galvanized iron box.

A condenser variable in steps of 0·002 mf. up to 0·2 mf. could have been built up from good quality Mansbridge condensers ; in the instrument described a condenser box



made by the Cambridge Scientific Instrument Company is in use.

The valve C and transformer D were mounted on a wooden box provided with an ebonite panel. The two "1500-turn" Igranic coils E were mounted in an adjustable coil holder. The valve used is of the dull-emitter type designed for resistance capacity coupling, having an impedance of 70,000 ohms and an amplification factor of 35. The "Multi-ratio" transformer made by Radio Instruments Ltd. was connected in the plate circuit so that the voltage applied to the bridge could be varied. To maintain the oscillation when the connexion to the bridge was broken a 0·01 mf. condenser F was placed in parallel with

the primary. A fuse G was inserted in the high tension lead.

The iron box containing the instrument acted as an efficient shield ; as an additional precaution the box was placed at a distance from the bridge and the connexion made by two lead-covered wires, the casing of which was connected to the box and to earth. The flash-lamp bulb H, mounted on the outside of the box, showed when the switch J was closed.

At high resistances the conductance of the cell due to the capacity between the plates is appreciable compared with the conductance of the electrolyte regarded as a pure resistance ; the true minimum can only be obtained if the capacities as well as the resistances are balanced by connecting a variable condenser of about 0·002 mf. across the resistance box. It is also convenient to connect a small condenser across the cell for making the final adjustment, since very accurate balancing of the capacities is necessary in order to secure a sharp minimum with high resistances.

Instead of the single Bell telephone frequently employed a pair of Brown A-type head-telephones were used, and no satisfactory results were obtained until the connexions to one ear-piece had been removed and joined together leaving only the other in circuit. If both are connected in series, as supplied, it is impossible to obtain complete silence at the null-point, the setting of the condensers is not sharp and the minimum is difficult to read. This is due to the fact that the body of the observer has a large capacity to earth.

In order to obtain a good wave-form free from harmonics the coupling between the coils should be as loose as possible. Oscillations of the right strength with a frequency of 1000 cycles were obtained with the coils almost at right angles, using 1·8 volts low tension, 160 volts high tension, a capacity in the oscillating circuit of 0·09 mf. and the 1 : 1 ratio of the transformer. The introduction of grid bias was found to be unnecessary.

When the condensers in the bridge circuit have been adjusted, the minimum is found to be as sharp and easy to read at 100,000 ohms as at 1000 ohms, and perfect silence is obtained at the null-point over the whole range of resistance. In order to show that the minimum so obtained was the true one, the frequency of the oscillator was varied, and no alteration in the position of the minimum was observed ; in every case the minimum was perfectly symmetrical. The same minima, but less easy to read, were obtained from the improved bridge circuit when the source of alternating

current was the Siemens' alternator previously in use in this laboratory.

We wish to express our thanks to Dr. Ulich for a detailed description of his apparatus and much valuable advice, and to Mr. C. E. G. Bailey of Balliol College for assistance with the mathematical theory of the apparatus.

The Physical Chemistry Laboratory,
Balliol College and Trinity College,
Oxford.
March, 1928.

CXVIII. *The Activity Coefficients of Hydrogen Chloride in Ethyl Alcohol.* *By* J. W. Woolcock, *B.A.*, *and* Sir Harold Hartley, *M.A.*, *F.R.S.*, *Balliol College, Oxford* *.

THE activity coefficients of hydrogen chloride in ethyl alcohol have been determined by Danner † and by Harned and Fleysher ‡. Danner measured the electromotive force of the cell

$$H_2/HCl \text{ in ethyl alcohol}/HgCl : Hg \quad . \quad . \quad (I.)$$

over the range of concentration 0·011 to 0·38 m. at 25° C., and Harned and Fleysher that of the cell

$$H_2/HCl \text{ in ethyl alcohol}/AgCl : Ag \quad . \quad . \quad (II.)$$

between 0·001 and 3·62 m. The results were shown by Harned and Fleysher to agree in the range 0·01 to 0·1 m. if 0·0350 volt is subtracted from Danner's results "to account for the difference in potential between the calomel and silver-silver chloride electrodes." This difference is, however, independent not only of the concentration but also of the solvent, provided that the solubilities of silver chloride and calomel are negligible compared with the concentration of the electrolyte, and has been shown to be 0·0467 volt in water § and in methyl alcohol ‖. If this value is employed there exists a discrepancy of about 12 millivolts between

* Communicated by the Authors.
† Journ. Amer. Chem. Soc. xliv. p. 2822 (1922).
‡ *Loc. cit.* xlvii. p. 82 (1925).
§ Linhart, *loc. cit.* xli. p. 1175 (1919). Horsch, *ibid.* p. 1790.
‖ Phil. Mag. l. p. 729 (1925).

the data of Danner and those of Harned and Fleysher, as has already been pointed out by Scatchard * and by Nonhebel and Hartley †.

In order to derive the numerical values of the activity coefficients from measurements of the electromotive force of cell (II.) it is first necessary to find the value of E_0 in the equation

$$E = E_0 - 0{\cdot}1183 \log f.c \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where f is the mean activity coefficient of the ions, and c is the concentration of the electrolyte in equivalents per litre. When accurate results are available in dilute solutions, it is possible to obtain E_0 without the aid of any auxiliary assumptions by plotting the function E_0', defined by the equation

$$E_0' = E + 0{\cdot}1183 \log c \quad . \quad . \quad . \quad . \quad . \quad (2)$$

against $c^{\frac{1}{2}}$ and extrapolating to infinite dilution.

The results of Danner extend only to 0·011 m., and those of Harned and Fleysher are stated by the authors to be unsuitable for direct extrapolation. The accuracy of the activity coefficients deduced by them must therefore depend on the validity of the auxiliary assumptions made in deducing E_0.

In the present investigation the electromotive force of cell (II.) has been redetermined at 25° C. in the concentration range 0·0003 to 1·2 m., with a view to obtaining values of the activity coefficient based on a value of E_0, arrived at by direct extrapolation. The data also serve to explain the discrepancy between the results of Danner and those of Harned and Fleysher.

Experimental.

The method employed was that used by Nonhebel ‡ in very dilute aqueous solutions, in which values of the electromotive force corresponding to a series of concentrations were obtained every time the cell was set up. This was done by starting with a known weight of pure alcohol in the cell and making successive additions of a solution of hydrogen chloride from a weight pipette. This type of cell is called a "dilution cell" to distinguish it from

* Journ. Amer. Chem. Soc. xlvii. p. 2098 (1925).
† Phil. Mag. l. p. 729 (1925).
‡ Phil. Mag. ii. p. 1085 (1926).

the ordinary H-cell which is filled with solution of known strength, and gives only one value every time it is set up. Each experiment is referred to as a "run."

Dilution cells have the advantage with aqueous solutions that the risk of contamination of the solutions by atmospheric impurities is decreased and several values are obtained in each run; it is therefore possible to recognize a faulty run by the lack of concordance among the points and lack of agreement with other runs in the range in which the concentrations overlap. For dilute solutions of non-aqueous solvents the dilution cell has the important additional advantage that it is possible to distinguish errors due to the presence of small traces of water from those due to other causes, since with these cells the amount of water does not change during the run, and consequently random errors due to faulty electrodes can be detected. The position of each set of values will show at once whether the alcohol contained any appreciable quantity of water, since 0·08 per cent. by weight of water raises the electromotive force of the cell by 8 millivolts at 0·01 m., and the effect increases with dilution.

Measurements of the viscosity were used as a routine method of detecting the presence of water in each sample of alcohol. The agreement of the results (0·01078 at 25° C.) with those of Goldschmidt and Aarflot * (0·01084 at 25° C.) and the concordance of the values for samples subjected to repeated purification indicated that only very small traces of water were present. This was confirmed by the agreement of the values obtained for the conductivity of solutions of hydrogen chloride with those of Goldschmidt †, and further evidence is to be found in the general concordance of the values of the electromotive force obtained by the authors and their agreement with those of Danner.

The method used for purifying the alcohol is based on the work of McKelvy ‡; the details have been worked out in this laboratory by Mr. E. D. Copley. The alcohol was first refluxed with freshly burnt lime and distilled through a Hempel column of the type described by Hartley and Raikes §. After treatment with aluminium amalgam, it was again distilled and a final distillation was made from a few grams of anhydrous copper sulphate in a current of

* *Zeits. phys. Chem.* cxxii. p. 371 (1926).
† *Loc. cit.* lxxxix. p. 129 (1915); *ibid.* cxiv. p. 1 (1924).
‡ Bull. Bur. Standards, xi. no. 3.
§ Journ. Chem. Soc. cxxvii. p. 524 (1925).

pure air. Its average specific conductivity was $0{\cdot}005 \times 10^{-6}$ reciprocal ohms.

The solutions were made by passing hydrogen chloride, generated by the action of strong sulphuric acid on pure dry sodium chloride, into ethyl alcohol. The apparatus used was constructed entirely of glass, and included a spray trap between the generator and absorber. The concentration of the solutions was determined by weight titration against baryta, methyl red being used as indicator ; the baryta was standardized against constant boiling aqueous hydrochloric acid *. The more dilute solutions were obtained by weight dilution.

If any esterification had taken place the effect of the water produced would have been more important than the change of concentration. The measurements of Kailan † of the rate of esterification of hydrogen chloride dissolved in ethyl alcohol show, however, that this cannot affect the results, provided that solutions are made up immediately before each experiment.

The cells were Jena flasks of 250 c.c. capacity, two of which (A and B) were employed in each run. A fully assembled cell is shown in fig. 1. The cells were cleaned, dried, closed with a ground glass stopper, weighed and re-weighed after filling with alcohol to just below the neck. The iridized gold hydrogen electrodes and the silver chloride electrodes were prepared in the manner described by Nonhebel and Hartley. The electrodes usually came rapidly to equilibrium with the solution, and the results of the run then showed good internal concordance ; on the other hand, in certain runs when equilibrium was attained slowly, the results were irregular and were rejected. In runs 9–12 satisfactory equilibrium values were never reached, and it was found necessary to remove completely the coating of iridium from the gold and to use a new iridium solution for plating the electrodes, when concordant results were again obtained.

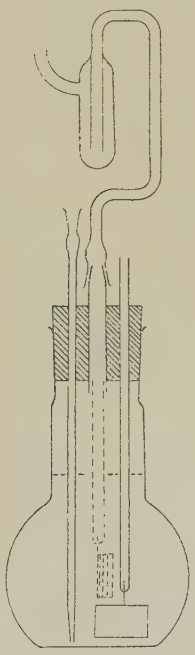
A hydrogen electrode and two silver chloride electrodes, which had stood in alcohol for 20 minutes, were inserted in a rubber bung which also held the hydrogen inlet and exit tubes. The rubber bungs had been freed from uncombined sulphur by treatment with caustic soda. The stopper of the

* Foulk and Hollingsworth, Journ. Amer. Chem. Soc. xlv. p. 1220 (1923).

† *Monatsh.* xxviii. p. 559 (1907).

Jena flask was removed and the rubber bung carrying the electrodes was at once inserted. The two cells A and B were mounted on a wooden frame, together with hydrogen saturators of the type described by Lewis, Brighton, and Sebastian *, and placed in a paraffin thermostat regulated to $25 \pm 0{\cdot}02°$ C. A stream of hydrogen generated electrolytically, freed from oxygen and dried by phosphorus pentoxide, was passed through the saturators into the cells.

Fig. 1.



The "Dilution" Cell.

Additions of solution were made by temporarily removing the hydrogen exit bubbler. Readings were begun two hours after the first addition of acid ; after each addition the cell was left until an electromotive force constant to 0·1 millivolt had been maintained for at least one hour.

In order to make concordance between runs as valuable a criterion of accuracy as possible, every run was carried out

* Journ. Amer. Chem. Soc. xxxix. p. 2245 (1927).

with a different sample of alcohol, a separately standardized solution of hydrogen chloride and freshly prepared electrodes.

Results.

Seventeen runs in all were carried out ; of these two were rejected on account of the presence of moisture in the alcohol, four failed owing to the poisoning of the iridium mentioned above, and two gave irregular results. The values of the electromotive force of the cells are given in Table I., the data for each run being grouped together. The number of the run, the cell, and the number of the point are shown in the first column ; for example, 2 A 1 indicates that this point was the first obtained from cell A in run 2. The second column gives the concentration in mols per 1000 grams of solvent. The third column gives the electromotive force of the cell corrected to 760 mm. pressure of hydrogen. The vapour pressure of ethyl alcohol solutions at 25° C. was taken as 59·0 mm.

Since dilution cells are not adapted for use at high concentrations, five determinations were carried out with two H-cells described by Nonhebel and Hartley, using solutions stronger than 0·1 m. ; these are distinguished by the letter H in the first column.

The results, together with those of Danner and Harned and Fleysher, are shown in fig. 2, where E is plotted against $\log m$. It will be seen that there is substanial agreement between our results and those of Danner except that the latter's two most dilute points are rather higher. Harned and Fleysher's value at 1·0 m. coincides with that obtained by us, but at higher dilutions their values are higher by as much as 10 millivolts at 0·1 m., 17 millivolts at 0·01 m. and 15 millivolts at 0·001 m. This supports the view of Scatchard that the alcohol used by Harned and Fleysher was not sufficiently dry, since the effect of water in raising the electromotive force increases in dilute solution.

In the second and third columns of Table II. the values calculated for $c^{\frac{1}{2}}$ and E_0' are given for points more dilute than 0·037 m. arranged in order of concentration. These data are plotted in fig. 3 together with similar values obtained by Danner and Harned and Fleysher in this range of concentration.

It will be seen that the relation between E_0' and $c^{\frac{1}{2}}$ is

approximately linear for values of $c^{\frac{1}{2}}$ less than 0·06; the value of E_0 obtained by direct extrapolation being $-0·0883 \pm 0·0003$ volt.

TABLE I.

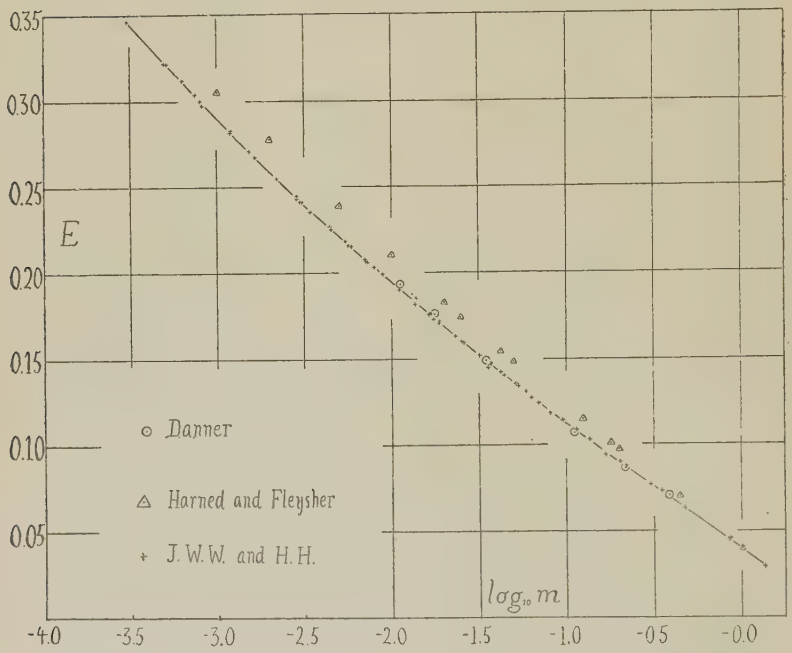
No.	*m*.	E.	No.	*m*.	E.
2A 1	0·002861	0·2447	8A 1	0·03621	0·1450
2A 2	0·007909	0·2034	8A 2	0·08100	0·1185
2B 1	0·005442	0·2185	8A 3	0·1677	0·0946
2B 2	0·01382	0·1856	8B 1	0·06342	0·1273
2B 3	0·02537	0·1601	8B 2	0·1147	0·1090
2B 4	0·05339	0·1345	8B 3	0·2031	0·0906
3A 2	0·007243	0·2067	13A 1	0·0004965	0·3221
3A 3	0·01673	0·1762	13A 2	0·001531	0·2710
3B 1	0·002963	0.2412	13A 3	0·003036	0·2417
3B 2	0·007103	0·2070	13A 4	0·004499	0·2252
3B 3	0·01643	0·1760	13B 1	0·0007990	0·3001
3B 4	0·02329	0·1636	13B 2	0·001190	0·2820
3B 5	0·03204	0·1522	13B 3	0·002193	0·2550
4B 1	0·0008175	0·2977	13B 4	0·003429	0·2357
4B 2	0·002862	0·2431	16A 1	0·04330	0·1404
4B 3	0·005613	0·2163	16A 2	0·06934	0·1248
6A 1	0·004401	0·2270	16A 3	0·1351	0·1032
6A 2	0·01872	0·1710	16A 4	0·2189	0·0880
6A 3	0·03703	0·1473	16A 5	0·3476	0·0734
6A 4	0·05165	0·1359	16A 6	0·4732	0·0636
6B 1	0·007007	0·2080	16B 1	0·09501	0·1146
6B 2	0·01379	0·1820	17A 1	0·0006297	0·3119
6B 3	0·02615	0·1594	17B 1	0·0003045	0·3466
6B 4	0·04246	0·1425	17B 2	0·0005158	0·3216
7A 1	0·005852	0·2156	17B 3	0·0007510	0·3040
7A 2	0·008863	0·1995	17B 4	0·001198	0·2827
7A 3	0·01114	0·1905	17B 5	0·001639	0·2677
7A 4	0·01749	0·1731	H 1	1·3427	0·0292
7A 5	0·02848	0·1552	H 2	1·0000	0·0405
7B 1	0·01875	0·1716	H 3	0·8429	0·0453
7B 2	0·03715	0·1477	H 4	0·8388	0·0451
7B 3	0·05188	0·1356	H 5	0·3000	0·0769
7B 4	0·05905	0·1311			

In non-aqueous solvents it is often more convenient to work in terms of weight normality than of volume normality, in which case the absence of density data will make it impossible to convert the results to a volume basis if the density of the solution differs appreciably from that of the

pure solvent. It is therefore simpler to use an activity coefficient corresponding to a concentration expressed in mols per 1000 grams of solvent ; this is usually denoted by γ. Nonhebel and Hartley calculated values of γ from their values of f by the relation

$$cf = a = m\gamma$$

Fig. 2.



where a is the activity referred to a standard state corresponding to the value of E_0 defined by the equation

$$E = E_0 - 0{\cdot}1183 \log cf.$$

This convention has the disadvantage that the limiting value of γ in dilute solution is numerically equal to the density of the solvent, while the limiting value of f is unity, since in such solutions $c/m = d$, where d is the density of the solvent. It is therefore preferable to define γ in terms of a standard state determined by the equation

$$E = E_0^m - 0{\cdot}1183 \log m\gamma.$$

The coefficients γ and f, which express the deviation of the properties of the solution from those of an ideal solution, will then both approach unity in the limit. In aqueous solutions the two standard states will be almost identical, but in other solvents the values of E_0 and E_0^m will differ by $0{\cdot}1183 \log d$.

TABLE II.

No.	$c^{\frac{1}{2}}$.	E_0'.	No.	$c^{\frac{1}{2}}$.	E_0'.
17B 1	0·01546	0·0818	7A 1	0·06778	0·0610
13A 1	0·01974	0·0812	6B 1	0·07416	0·0593
17B 2	0·02012	0·0797	3B 2	0·07466	0·0596
17A 1	0·02224	0·0792	3A 2	0·07540	0·0589
17B 3	0·02428	0·0780	2A 2	0·07879	0·0577
13B 1	0·02505	0·0788	7A 2	0·08341	0·0558
4B 1	0·02534	0·0800	7A 3	0·09353	0·0530
13B 2	0·03057	0·0764	6B 2	0·1040	0·0506
17B 4	0·03067	0·0753	2B 2	0·1041	0·0489
13A 2	0·03467	0·0745	3B 3	0·1135	0·0475
17B 5	0·03588	0·0742	3A 3	0·1146	0·0464
13B 3	0·04148	0·0720	7A 4	0·1171	0·0472
2A 1	0·04739	0·0686	7B 1	0·1212	0·0451
4B 2	0·04740	0·0702	6A 2	0·1212	0·0458
3B 1	0·04823	0·0703	3B 4	0·1352	0·0420
13A 3	0·04883	0·0686	2B 3	0·1411	0·0411
13B 4	0·05189	0·0683	6B 3	0·1432	0·0402
6A 1	0·05878	0·0642	7A 5	0·1496	0·0400
13A 4	0·05943	0·0649	3B 5	0·1585	0·0370
4B 3	0·06331	0·0624	6A 3	0·1705	0·0345
2B 1	0·06537	0·0618	7B 2	0·1797	0·0339

Table III. gives the molal activity coefficients at round concentrations calculated in this way for solutions of hydrogen chloride in water, methyl alcohol, and ethyl alcohol.

Table IV. gives the values of the free energy of transfer of hydrogen chloride from ethyl and methyl alcohol to water calculated from the above data.

It is of interest to see whether the values obtained for the activity coefficient of hydrogen chloride are in agreement with the theory of Debye and Hückel *, which in very dilute solutions leads to the limiting equation

$$-\log f = Ac^{\frac{1}{2}}$$

* *Phys. Zeits.* xxi. p. 185 (1923); xxv. p. 97 (1924).

Fig. 3.

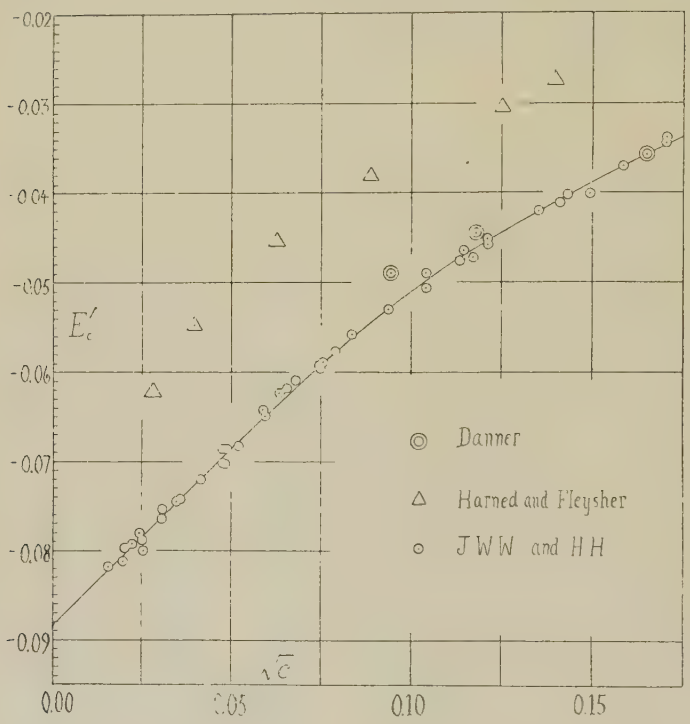


TABLE III.

m.	Ethyl alcohol.	Methyl alcohol.	Water.
0·0005	0·851	0·953	0·981
0·001	0·800	0·912	0·973
0·002	0·731	0·867	0·962
0·005	0·622	0·813	0 942
0·01	0·518	0·745	0·919
0·02	0·426	0 664	0·889
0·05	0·317	0·541	0·841
0·1	0·253	0·461	0·807
0·2	0·198	0·386	0·779
0·5	0·140	0·289	0·768
1·0	0·103	...	0·822

TABLE IV.

The Free Energy of Transfer of HCl from Alcohol to Water.

m in both solutions.	$-\Delta F$ (in calories).	
	EtOH to H_2O.	MeOH to H_2O.
0·001	6683	5256
0·01	6209	5076
0·1	5521	4670
0·5	4855	4253
1·0	4434	.....

where A is a constant depending on the temperature, the dielectric constant of the solvent and certain universal constants. For hydrogen chloride in ethyl alcohol, as in water and methyl alcohol, the curve obtained by plotting the values of $-\log f$ against $c^{\frac{1}{2}}$ becomes linear in dilute solutions in conformity with the theory. This can be seen in fig. 3, for since

$$E_0' = E + 0{\cdot}1183 \log c,$$

and

$$E = E_0 - 0{\cdot}1183 \log cf,$$

$$E_0' = E_0 - 0{\cdot}1183 \log f,$$

and therefore as E_0' has a linear relationship to $c^{\frac{1}{2}}$ the same is true of $-\log f$.

The value of A calculated from the Debye theory at 25° C is for water 0·505, for methyl alcohol 2·10, and ethyl alcohol 2·79. The observed values of A in water and methyl alcohol are 0·39 and 1·485, which agree more closely with the coefficient of Milner * than of Debye. Scatchard †, however, points out that the experimental results can be reconciled with the Debye value of A if the complete Hückel ‡ equation

$$-\log f = \frac{Ac^{\frac{1}{2}}}{1 + \alpha c^{\frac{1}{2}}} - Bc$$

is used to obtain E_0. This equation contains two additional

* Phil. Mag. xxiii. p. 551 (1912); xxv. p. 743 (1913).
† Phil. Mag. ii. p. 577 (1926).
‡ *Phys. Zeits.* xxvi. p. 93 (1925).

constants α and B, of which α is proportional to the radius of the ions and B is a function of the change of dielectric constant with concentration. In practice α and B are evaluated empirically. In ethyl alcohol the experimental value of A is 3·40, which is larger than the Debye theory predicts. The use of the Hückel equation would only make the lack of agreement more pronounced, unless a negative value were given to α, corresponding to a negative ionic radius.

The basic assumption of the Debye-Hückel theory is complete dissociation, and the most probable explanation of the discrepancy in the value of A in the case of ethyl alcohol is that even in dilute solutions an appreciable quantity of hydrogen and chlorine ions are associated to form molecules. Evidence for this is seen in the much lower values of the activity coefficient in solutions in ethyl alcohol than in solutions in water or methyl alcohol, and in the larger vapour pressure of hydrogen chloride in ethyl alcohol solutions. Experiments in progress in this laboratory on the conductivity of salts and acids in ethyl alcohol afford additional evidence that dissociation may not be complete even at very high dilutions.

Summary.

1. The activity coefficients of solutions of hydrogen chloride in ethyl alcohol have been obtained by measurements of the electromotive force of the cell $H_2/HCl/AgCl : Ag$ at 25° C.

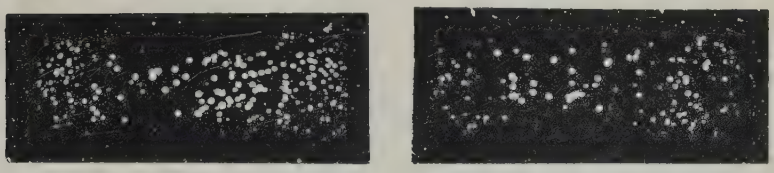
2. A comparison has been made with the results obtained by Danner and by Harned and Fleysher.

3. The equation $-\log f = 3{\cdot}40c^{\frac{1}{2}}$ has been found to represent the course of the activity coefficient in the range 0·0003 m. to 0·004 m., the value of the coefficient being greater than that demanded by the Debye theory. It is suggested that this is due to incomplete dissociation.

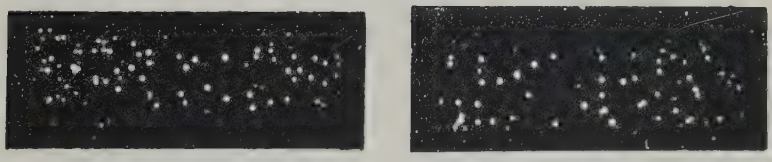
Physical Chemistry Laboratory,
Balliol College and Trinity College,
Oxford.
March 1928.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

Droplets formed by Condensation on Nuclei emitted by a hot Platinum Wire.



$14{\cdot}5 \times 10^3$ nuclei per c.c.



$7{\cdot}95 \times 10^3$ nuclei per c.c

Total magnification $\times$ 13

FIG. 3.

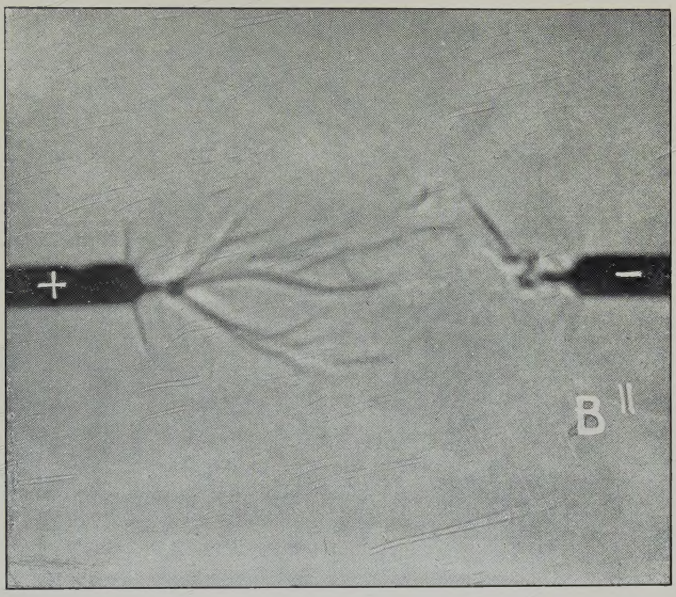


FIG. 4.

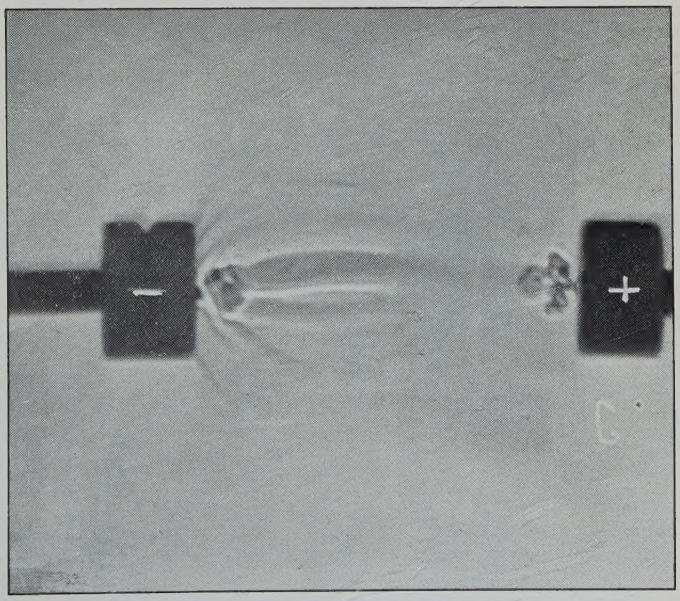


Fig. 5.

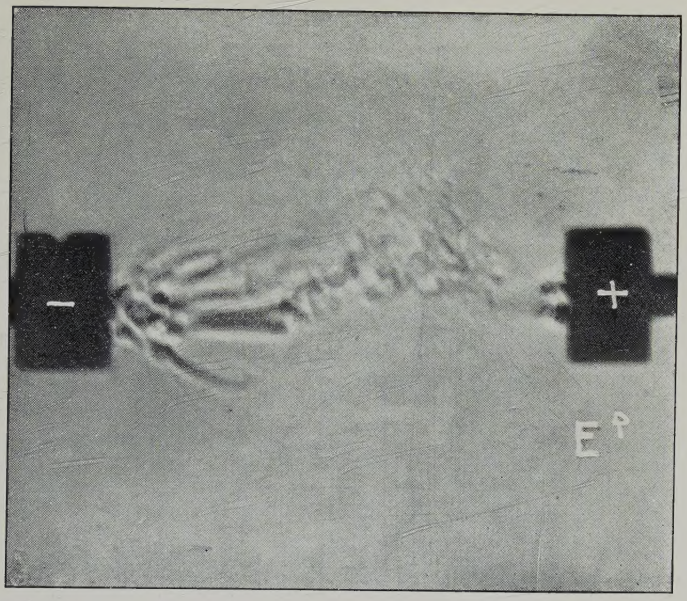


Fig. 6.